Valorisation of Indonesian plant oil resources

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To my parents

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Summary

In future bio-based societies, biomass is the feedstock of choice for the production of energy, transportation fuels, chemicals, and materials. Benefits compared to the current fossil-based economies are, among others, reduction of CO_2 emissions in the environment and less or no dependency of diminishing fossil resources. In addition, the transition from fossil- to bio-based societies will create new economic activities and provide ample opportunities for biomass rich countries such as Indonesia. In such bio-based societies, traditional oil refineries are replaced by the so called biorefineries, in which biomass is used as the input and converted in an integrated and energy and material efficient manner to bio-based chemicals, bio-fuels, and bio-energy (Figure 1).

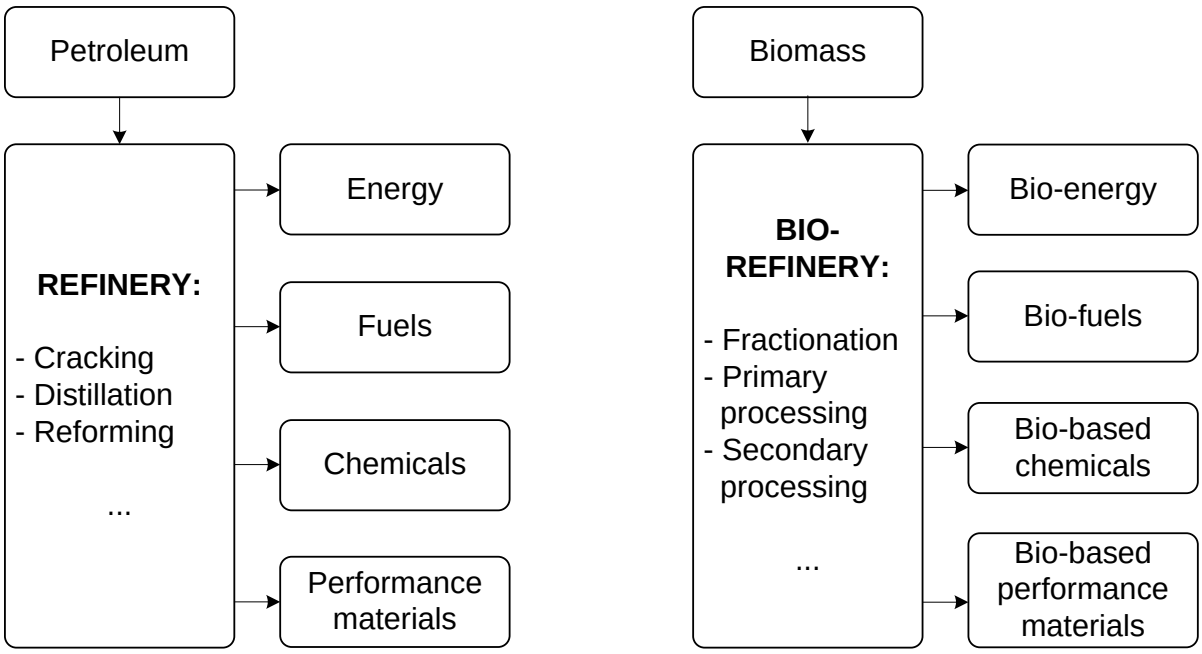


Fig. 1 Oil- and bio-refinery units

In bio-based societies, careful selection of the biomass sources is of pivotal importance and will ultimately determine the sustainability of the conversion chains. Competition with food products should be avoided and as such preferably woody biomass, agricultural waste product, or aquatic biomass (micro- and macro algae) are used. In this respect, non-edible plant oils are also attractive biomass feedstocks, though direct and indirect land use aspects should be carefully considered.

Jatropha curcas L. is an example of an oil-bearing plant that produces a toxic oil, unsuitable for human consumption. The plant is well known in many tropical countries like Indonesia. It has potential to become an important oil producing plant in the future, though many techno- and socio-economical hurdles will need to be taken before large scale production will become attractive. The plant oil extracted from its seeds is a potential feed for biofuels as well as oleochemicals. Examples are the conversion of the oil to biodiesel and jet fuel. Particularly the latter application is investigated in detail by the aviation sector at the moment (KLM, Boeing, Airbus). However, when applying the biorefinery concept, all plant parts need to be valorised and not only the plant oil. Also in this respect, the Jatropha *curcas* L. offers ample opportunities. The remaining part of the seeds after oil extraction is rich in proteins, carbohydrates, and lignin. These components are interesting starting materials for the production of bio-based chemicals and performance materials. In addition, various plant parts contains interesting bio-active component that could be of interest for the pharmaceutical industry.

Besides *Jatropha curcas* L., the *Sterculia foetida* L. also produces an attractive non-edible oil and as such is also an interesting plant source for further valorisation studies on Indonesian resources. In this case, the oil is of particular interest as the fatty acid chain contains a very reactive functional group in the form of a cyclopropene unit.

The seeds of the *Jatropha curcas* L. and the *Sterculia foetida* L. are the starting materials for the research described in this thesis (Fig. 2).

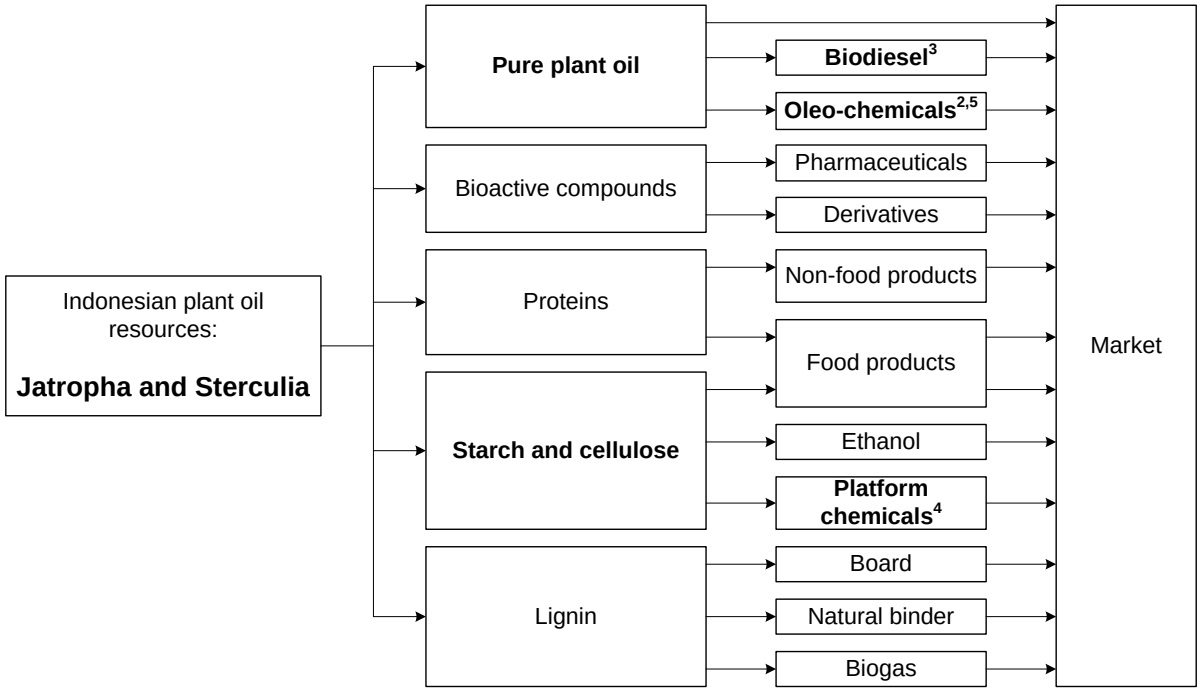


Fig. 2 Bio-refinery of the *Jatropha curcas* L. and *Sterculia foetida* L. (superscripts: the corresponding chapter numbers in this thesis)

In **chapter 2**, the synthesis and properties of a number of novel branched *Jatropha curcas* L. oil (JO) derivatives containing vicinal di-ester units in the fatty acid chains are reported. Both the length (acetyl vs. hexanoyl) and the stereochemistry of the vicinal di-ester units (*cis* vs. *trans*) were varied. The compounds were prepared by two different synthetic approaches using catalytic chemistry. The first approach involves epoxidation of JO using a Sharpless epoxidation with methyltrioxorhenium as the catalyst to give epoxidised JO, followed by an esterification reaction with the corresponding anhydrides using ammonium-12-molybdophosphate (AMP) as catalyst to give *trans*- di-esters of JO. The second approach is based on the dihydroxylation of JO using either the Prilezhaev method, resulting in *trans*-diols of JO, or the Upjohn method using osmium tetroxide as catalyst to give *cis*-diols of JO. In subsequent steps, the diols were esterified with acetic- or hexanoic anhydride using dimethylaminopyridine as catalyst to the corresponding *cis*- and *trans*- di-esters of JO. The best cold flow properties (lowest pour- and cloud point, crystallisation and melting temperature) were obtained for JO with hexanoyl branches in a *trans* orientation (pour point of -14 ^{o}C, melting point of -5 ^{o}C, and crystallisation temperature of -25 ^{o}C) and these values are considerably better than for the JO source.

In **chapter 3**, an experimental study on the application of metal triflate salts for the (*trans*-) esterification of fatty esters (triolein, methyl oleate, methyl linoleate), a fatty acid (oleic acid), as well as *Jatropha curcas* L. oil with methanol and higher alcohols (ethanol, n-propanol, *iso*-propanol, *iso*-butanol, *tert*-butanol) is described. The effects of metal type (scandium, bismuth, aluminium, lanthanum, copper, zinc) and process conditions on reaction performance were evaluated. Highest conversions were obtained with $Al(OTf)_3$. Reaction of triolein with methanol gave 99 mol% conversion at 165 ^{o}C for 1 h reaction time and the main product was the methyl ester. In addition, partial methoxylation of the carbon-carbon double bonds in the fatty acid chains was observed, though the yield was less than 20 mol%. The *trans*-esterification reaction was also successfully performed using higher alcohols, giving > 95 mol% conversions for ethanol, n-propanol, *iso*-propanol, and *iso*-butanol, whereas *tert*-butanol was not reactive. For the reaction of oleic acid with methanol, quantitative esterification, partial methoxylation of the carbon-carbon double bonds and the formation of small amounts of a lactone was observed. The methodology using $Al(OTf)_3$ was successfully performed on the *trans*-esterification reaction of JO (FFA content of 2.1 wt%) with various alcohols. Key properties (viscosity, pour- and cloud points) of the (branched) Jatropha oil esters were determined. The best cold flow properties were obtained for the *iso*-propyl esters of JO, with cloud point (CP) and pour point (PP) of -3 and -24 ^{o}C, respectively.

In **chapter 4**, an exploratory study on the catalytic oxidation of levulinic acid (LA) and feeds capable of generating LA *in situ* (e.g. Jatropha seed shells) to succinic acid (SA) is reported using a wide range of homogeneous catalysts. Sulphuric acid in combination with hydrogen peroxide in acetonitrile was found to be the best catalytic system giving a SA selectivity of 73 mol% at 55 mol% LA conversion (80 ^{o}C, 0.5 M H_2SO_4 and a 5 fold excess of aqueous H_2O_2). Besides SA, malonic acid (MA), acetic acid (AA), and formic acid (FA) were formed as well. The catalytic system was also explored for the oxidation of furfural and other relevant abundantly available biopolymers (starch, cellulose), their hydrolysed monomers (D-glucose and xylose) and a lignocellulosic biomass source in the form of *Jatropha curcas* L. (JCL) seed

shells. For furfural, a SA yield of about 40 mol% at full furfural conversion was obtained in water (105 ^{o}C). A two-step approach was applied for glucose, cellulose, xylose, and starch, involving the acid catalysed hydrolyses in water to LA and/or furfural followed by the subsequent oxidation using hydrogen peroxide. Highest SA yield (23 mol% on LA in hydrolysate, 10 mol% on substrate) were obtained for D-glucose. For JCL seed shells, the SA yield was 25 mol% (based on LA in the hydrolysate, 6 mol% based on the C6 sugar content in the feed).

Finally, in **chapter 5**, an experimental study to modify *Sterculia foetida* L. oil (STO) or the corresponding methyl esters (STO FAME) to ester derivatives with branches in the fatty acid chains is reported. The transformations involve conversion of the cyclopropene rings in the fatty acid chains of STO through various catalytic as well as stoichiometric reactions. Full conversion of the cyclopropene rings was obtained using Diels-Alder chemistry involving cyclopentadiene in water at 40 ^{o}C without the need for a catalyst. Olefin metathesis reactions were performed using a Grubbs 2nd generation catalyst and cyclopropene ring conversion was ≥ 99 mol% and 54 mol% with 2,3-dimethyl-2-butene and 1-octene, respectively. Oxidation reactions were performed using established epoxidation (Sharpless) and dihydroxylation (Prilezhaev) protocols using aqueous hydrogen peroxide as the oxidant. For both reactions, full conversion of the cyclopropene rings was obtained at room temperature to yield the corresponding α,β-unsaturated ketone in good selectivities. Rearrangement reactions of the cyclopropene rings to the corresponding conjugated diene were successfully performed using homogeneous and heterogeneous palladium catalysts. Excellent conversions (≥ 99 mol%) were obtained using homogeneous palladium catalyst in a biphasic cyclohexane-water mixture (1:1) at 90 ^{o}C. Relevant cold flow properties of all products were determined and compared to crude STO and STO FAME. Best results were obtained for the metathesis products of STO with 1-octene, with a cloud point (CP) and pour point (PP) of -12 ^{o}C.

Samenvatting

In een toekomstige groene samenleving is biomassa de uitgelezen grondstof voor de productie van energie, transport brandstoffen, chemicaliën, en materialen. Voordelen van het gebruik van biomassa ten opzichte van conventionele fossiele bronnen zijn onder andere een geringere CO_2 uitstoot en een kleinere of zelfs geen afhankelijkheid meer van deze fossiele grondstoffen. Daarnaast zal de overgang van fossiel naar biomassa nieuwe economische activiteiten creëren, met name voor landen rijk in biomassa, zoals bijvoorbeeld Indonesië. In toekomstige groene samenlevingen zullen traditionele olieraffinaderijen vervangen worden door zogenaamde bio-raffinaderijen, eenheden waar biomassa op een geïntegreerde en materiaal- en energie efficiënte wijze wordt ingezet voor het maken van groene chemicaliën, biobrandstoffen, en groene energie (Figuur 1).

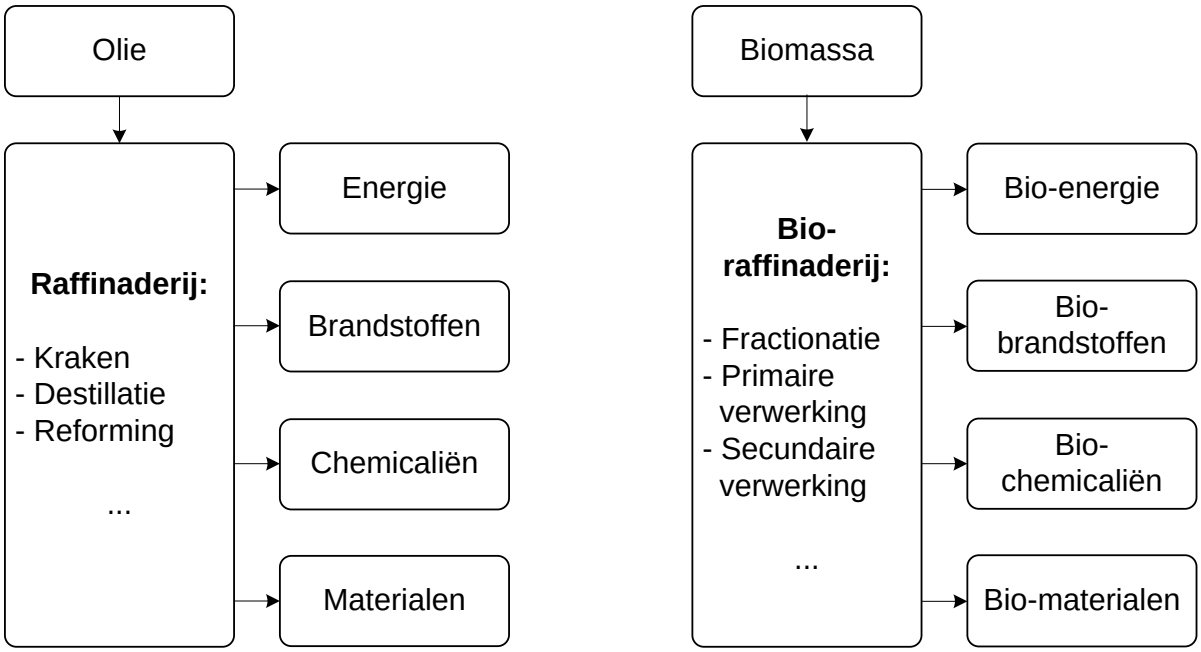


Fig. 1 Olieraffinaderijen en bio-raffinaderijen

In een groene samenleving is een zorgvuldige keuze van de biomassa voedingen van groot belang en zal uiteindelijk de duurzaamheid van de productieketen bepalen. Competitie met voedsel moet vermeden worden en daarom wordt bij voorkeur hout, landbouw residuen, of aquatische biomassa (algen en zeewier) gebruikt. Vanuit dit oogpunt zijn niet eetbare plantaardige oliën ook interessante grondstoffen hoewel de directe en indirecte gevolgen van het

landgebruik voor het telen van dergelijke gewassen goed in kaart gebracht moeten worden.

Jatropha curcas L. is een voorbeeld van een oliehoudende plant die een giftige olie produceert die ongeschikt is voor menselijke consumptie. De plant komt voor in een groot aantal tropische landen waaronder Indonesië. Het heeft de potentie om in de toekomst een belangrijk oliehoudend gewas te worden, hoewel er nog een flink aantal technische- en economische hordes genomen moeten worden voordat productie op grote schaal aantrekkelijk wordt. De olie die uit de zaden gewonnen wordt, kan gebruikt worden als grondstof voor biobrandstoffen en groene chemicaliën. Voorbeelden zijn de omzetting van de olie in biodiesel en bio-kerosine. Laatstgenoemde toepassing wordt op dit moment uitgebreid onderzocht door de luchtvaartindustrie (o.a KLM, Boeing en Airbus). Echter in een bio-raffinaderij moeten alle delen van een plant gebruikt worden en niet alleen de olie. Wat dat betreft zijn er voor de *Jatropha curcas L.* genoeg mogelijkheden. De perskoek, het residu nadat de olie uit de zaden is gehaald, is rijk aan eiwitten, suikers en lignine. Deze componenten zijn interessante grondstoffen voor de productie van groene chemicaliën en hoogwaardige materialen. Daarnaast bevatten verschillende delen van de plant bio-actieve componenten die interessant kunnen zijn voor de farmaceutische industrie.

Sterculia foetida L. produceert net als de *Jatropha curcas L.* een aantrekkelijke, niet eetbare olie en is in die hoedanigheid ook een interessante plant voor verdere valorisatie studies. Het interessante van deze olie is de aanwezigheid van een zeer reactieve cyclopropeen groep in de vetzure ketens van de olie die interessante chemische modificatie mogelijkheden biedt.

De zaden van de *Jatropha curcas L.* en de *Sterculia foetida L.* zijn de uitgangsmaterialen voor het onderzoek beschreven in dit proefschrift (Figuur 2).

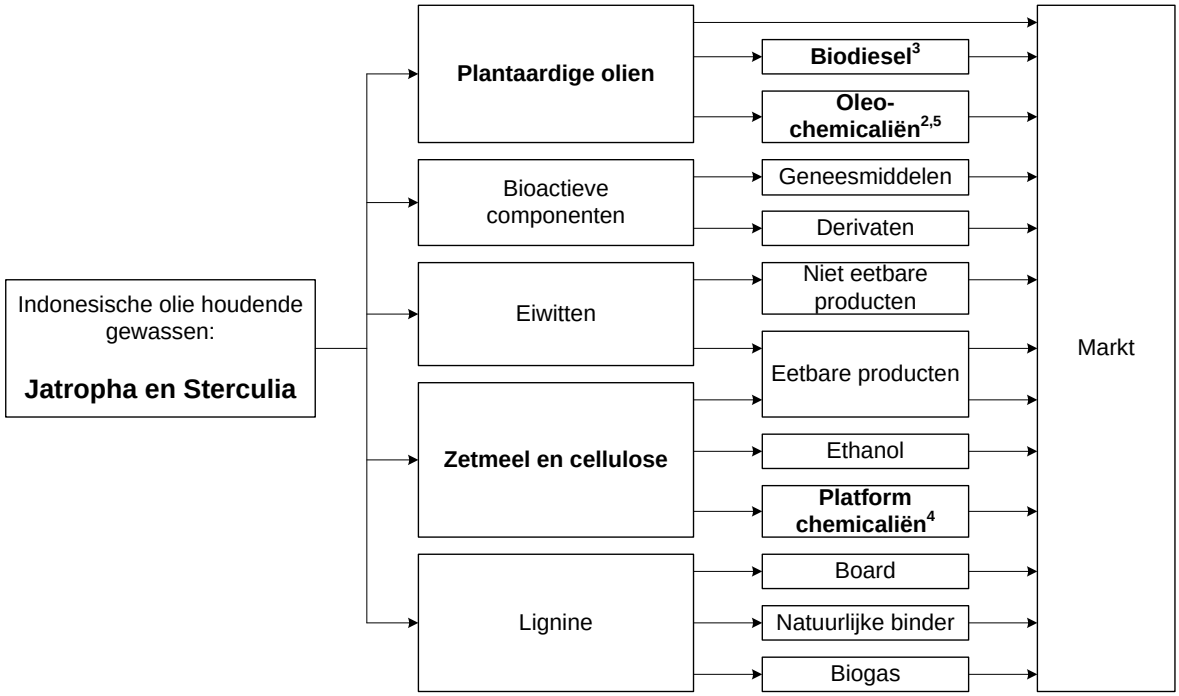


Fig. 2 *Jatropha curcas L.* en *Sterculia foetida L.* bio-raffinaderij (in superschrift, de nummers van de overeenkomstige hoofdstukken in dit proefschrift).

In **hoofdstuk 2** worden de synthese en de eigenschappen van een aantal nieuwe vertakte derivaten van *Jatropha curcas L.* olie (JO) beschreven. Deze derivaten bevatten vicinale di-ester groepen in de vetzure ketens. De lengte van de estergroepen is gevarieerd door azijnzuur of hexaanzuur groepen te gebruiken. Tevens is de stereochemische orientatie van de vicinale ester groepen gevarieerd door gebruik te maken van verschillende katalysatoren en synthese routes.

Met behulp van een Sharpless epoxidatie met methyl trioxorhenium als katalysator zijn de C-C dubbele bindingen geepoxideerd. De geëpoxideerde JO is vervolgens veresterd met anhydrides en ammonium-12-molybdophosphate als katalysator tot *trans* di-esters. De tweede route omvat de dihydroxylatie van JO tot *trans*- (Prilezhaev methode) en *cis*-diolen (Upjohn methode met osmium tetroxide als katalysator). Deze diolen zijn veresterd met azijn- en hexaanzuur anhydride en dimethylaminopyridine als katalysator om de overeenkomstige *cis*- en *trans*- di-esters van JO te synthetiseren.

De zogenaamde 'cold flow' eigenschappen zoals de kristallisatie- en stolling temperatuur van de verschillende derivaten zijn bepaald. De beste eigenschappen zijn gevonden voor JO met hexaan ester vertakkingen in de *trans* oriëntatie. De 'cold flow' eigenschappen van dit derivaat (stol temperatuur -14 ^{o}C, smeltpunt -5 ^{o}C en kristallisatie temperatuur -25 ^{o}C) zijn een beduidend beter dan die van de ruwe Jatropha olie.

In **hoofdstuk 3** is een experimentele studie beschreven naar het gebruik van metaal triflaat katalysator voor de (*trans*-) esterificatie van vetzuren en vetzure esters met diverse alcoholen. Het effect van het type metaal (scandium, bismut, aluminium, lanthaan, koper, en zink) en de procescondities op de conversies en product selectiviteit zijn bepaald. De hoogste conversies zijn behaald met $Al(OTf)_3$. De reactie van triolein met methanol gaf 99 mol% conversie bij 165 ^{o}C na 1 uur reactie tijd, het voornaamste product was de methyl ester. Daarnaast werd een gedeeltelijke (<20 mol%) methoxylatie van de C-C dubbele bindingen in de vetzure ketens waargenomen. De *trans* esterificatie reactie werd ook succesvol uitgevoerd met hogere alcoholen. Conversies van meer dan 95 mol% zijn behaald met ethanol, *n*-propanol, *i*-propanol en *i*-butanol. *t*-Butanol was niet reactief onder de geteste omstandigheden. Bij de reactie van oliezuur met methanol werd volledige esterificatie waargenomen en een gedeeltelijke methoxylatie van de dubbele bindingen en de formatie van kleine hoeveelheden van een lacton. Jatropha olie, met een vrij vetzuur gehalte van 2.1 mol%, is succesvol veresterd met verschillende alcoholen met $Al(OTf)_3$ als katalysator. De viscositeit, stol- en de kristallisatie temperatuur van de (vertakte) Jatropha esters zijn bepaald. De beste 'cold flow' eigenschappen zijn verkregen voor de isopropyl esters van JO en gaven een kristallisatie temperatuur van -3 ^{o}C en een stol tempratuur van -24 ^{o}C.

In **hoofdstuk 4** wordt een exploratieve studie naar de katalytische oxidatie van levuline zuur (LA) en biomassa bronnen die in *situ* LA kunnen produceren (bijvoorbeeld de schillen van Jatropha zaden) naar barnsteenzuur (SA) beschreven. Een breed scala aan homogene katalysatoren is getest en een combinatie van zwavelzuur en waterstofperoxide in acetonitril geeft het beste resultaat. Een SA selectiviteit van 73 mol% bij 55 mol% LA conversie werd bereikt met 0.5 M H_2SO_4 en een vijfvoudige overmaat H_2O_2 in water bij 80 ^{o}C. Naast SA worden ook malonzuur, azijnzuur en mierenzuur gevormd.

Dit katalysator systeem is ook gebruikt voor de oxidatie van furfural en veelvoorkomende biopolymeren zoals zetmeel en cellulose. Ook zijn D-glucose en xylose en de schillen van Jatropha zaden getest. In het geval van furfural, werd een SA opbrengst van ongeveer 40 mol% bereikt bij volledige conversie van de furfural (105 ^{o}C in water). Een tweestaps benadering is toegepast voor D-glucose, cellulose, xylose, en zetmeel. Hierbij werd de uitgangstof eerst in water gehydrolyseerd naar LA en/of furfural, gevolgd door de oxidatie met waterstofperoxide. De hoogste opbrengst aan SA (23 mol% ten opzichte van de LA gevormd in de eerste stap, 10 mol% van de uitgangstof) is gevonden voor D-glucose. Voor de schillen van de Jatropha zaden bedroeg de SA opbrengst 25 mol% van de LA gevormd in de eerste stap en 6 mol% gebaseerd op het gehalte aan C6 suikers in de grondstof.

In **hoofdstuk 5**, wordt een experimentele studie gerapporteerd om *Sterculia foetida L.* olie (STO) of de methyl esters van deze olie (STO FAME) te modificeren tot ester derivaten met vertakkingen in de vetzure keten. Deze vertakkingen zijn geïntroduceerd door zowel katalytisch als stoichiometrisch reacties met de cyclopropeen ringen in de vetzure keten. Volledige conversie van de cyclopropeen ringen werd bereikt met cyclopentadieen in een ongekatalyseerde Diels-Alder reacties in water bij 40 ^{o}C. Olefine metathese reacties zijn uitgevoerd met een Grubbs 2^{e} generatie katalysator en 2,3-dimethyl-2-buteen en 1-octeen als olefines. De conversie van de cyclopropeen ringen is meer dan 99 mol% voor 2,3-dimethyl-2-buteen en 54 mol% bij het gebruik van de terminale alkeen. Oxidatie reacties met waterstofperoxide zijn uitgevoerd volgens bekende epoxidatie (Sharpless) en dihydroxylatie (Prilezhaev) protocollen. Beide reacties geven volledige conversie van de cyclopropeen ringen bij kamertemperatuur met een goede selectiviteit voor een α,β-onverzadigde keton. Reacties om de cyclopropeen ring om te leggen tot het overeenkomstige geconjugeerde diëen zijn succesvol uitgevoerd met homogene en heterogene palladium katalysatoren. Zeer goede conversies (meer dan 99 mol%) zijn bereikt met een homogene palladium katalysator in een twee fasen vloeistof systeem (cyclohexaan en water (1:1) bij 90 ^{o}C). Relevante 'cold flow' eigenschappen zijn bepaald en vergeleken met ruwe STO en STO FAME. De beste resultaten werden bereikt met de metathese producten van STO en 1-octeen, met een kristallisatie- en stol temperatuur van -12 ^{o}C.

Chapter 1

Introduction

1.1 Bio-based economies

A bio-based economy is an economy that uses biomass instead of fossil resources for the production of energy, transportation fuels, and chemicals. In addition, these activities should be carried out with a minimum energy use and zero waste of materials by re-using them *in situ* or in the ecosystem. A more comprehensive definition has been given by the European Commission, Directorate General of Research and Innovation for Food, Agriculture and Fisheries, and Biotechnology and states that a bio-based economy is "*a low waste production chain starting from the use of land and sea, through the transformation and production of bio-based products adapted to the requirements of end-users. It integrates the full range of natural and renewable biological resources — land and sea resources, biodiversity and biological materials (plant, animal, and microbial), through to the processing and the consumption of these bio-resources*" [1]. Table 1 provides benefits and potential issues that may arise from the application of the bio-based economy concept.

Table 1 Benefits and potential problems of bio-based economies [1]

Benefits	**Potential problems**
Reduction of CO_2 emissions	Food supply versus biomass production
New business opportunities and job market opening	Over exploitation of natural resources
Resilient and sustainable food chains	Loss of biodiversity
Development of science based communities and stimulating high-skilled jobs	Climate change
	Societal issues

The anticipated reductions in CO_2 emissions is a strong driver for the introduction of bio-based economies and is due to the fact that feeds are in majority from renewable resources (biomass). The transition from the current crude oil based economies to bio-based economies will require major inventions and innovations and lead to new business opportunities.

Stronger demands for biomass for non-food applications may result in higher biomass prices and as such affect the global food industry. As such, there is a strong incentive to develop bio-based economies that definitively will not lead to **food** versus **fuel/material** and **land use** issues. In this respect, careful selection of the biomass feeds is of prime importance for the sustainable introduction of the bio-based economy concept.

1.2 Biomass valorisation

1.2.1 What is biomass

Biomass is defined as "*any organic matter that is available on a renewable basis, including dedicated energy crops and trees, agricultural food and feed crop residues, aquatic plants, wood and wood residues, animal wastes and other waste materials*" [2]. The major components of biomass include carbohydrates (cellulose, hemicellulose, and starch), lignin (an aromatic rich thermoset), lipids (fats, waxes, oils), proteins, and ash (minerals) [3]. The first four basic components have high application potential for use as feeds in future bio-based chemical industries [4].

Annually, biomass is produced at an estimated value of 170 x 10^9 tonnes. About 75% consists of carbohydrates, mainly in the form of cellulose, hemicellulose and starch, 20% is lignin, and the remaining 5% are fats and oils, proteins, and other substances [5]. Table 2 presents some representative examples of biomass sources and their chemical composition.

Table 2 Average chemical composition of representative biomass sources (d.b.,wt%)

Lignocellulose- and starch-based plants							
Plant	*Cellulose*	*Hemi-cellulose*	*Protein*	*Lignin*	*Extractives (starches, terpenes)*	*Ash*	*Ref*
Corn stover	36	23		17	6	10	6
Switch grass	42	32	8	12	0	6	6
Sugarcane	22	15		11	43	9	6
Sweet sorghum	35	17		17	23	5	6
Eucalyptus	48	14		29	2	1	6
Pine	48	21		25	3	0	6

Triglyceride-producing plants						
Plant	*Oil*	*Protein*	*Carbohydrate*	*Fiber*	*Ash*	*Ref*
Palm (fruit bunch)	24					7
Soybean	20	40	29	5	6	8,9
Rapeseed	39	40				8,10
Sunflower	45	20	10	21	4	11,12
Coconut	68	7	15	6	4	13
Palm kernel	52	9	28	9	2	13
Cottonseed	35	39				14
Peanut	45	50				8,15
Olive	27					8
Corn grain	5	5	75	15		16
Rice bran	18	12	45	20	5	17
Safflower	35					17

Algae							
Species	*Oil*	*Protein*	*Carbohydrate*	*Glycerol*	*Ash*	*unknown*	*Ref*
Botryococcu braunii	45	22	14	0	6	13	6
Dunaliella bardawil	10	10	40	16	15	9	6
Dunaliella salina	25	29	16	9	9	12	6
Ankistrodesmus sp.	25	31	11	0	5	28	6
Isochrysis sp.	7	37	11	0	12	33	6
Nanochloris sp.	21	33	13	0	14	19	6
Nitzschia sp.	12	17	9	0	20	42	6

The carbohydrate fraction in lignocellulosic biomass consists of two basic components: cellulose and hemicellulose. Cellulose consist of glucose, a C6 sugar, while hemicellulose consists of C5 and C6 sugars, examples are glucose, mannose, galactose, arabinose, and xylose [18].

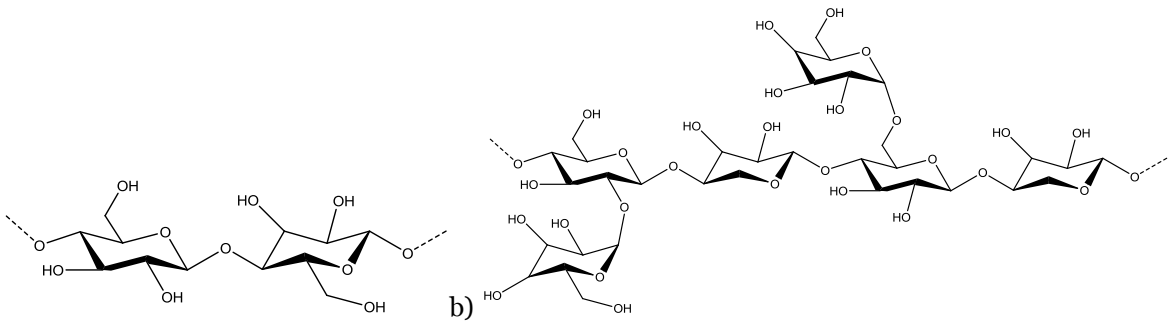


Fig. 1 Carbohydrates fraction: a) cellulose, b) hemicellulose

Lignin is a complex network made up of multi-substituted arylpropane, and hydroxyphenol units [4], see Fig. 2. Lignin is the “glue” that binds the cellulose and hemicellulose in plant fibers to provide structure and strength. The three basic phenolic compounds used by plants/trees to synthesise lignin are *p*-coumaryl alcohol, *p*-conyferyl alcohol, and *p*-sinapyl alcohol [19].

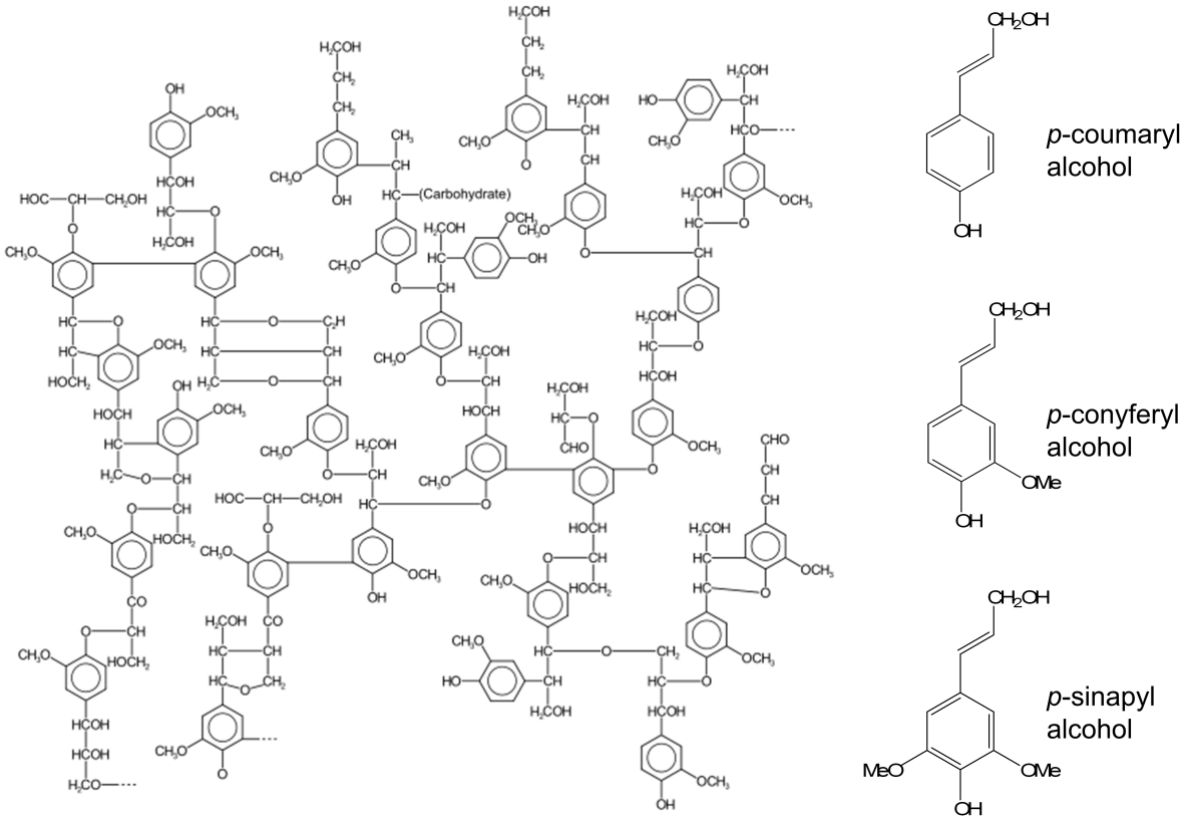


Fig. 2 Chemical structure of lignin and its building blocks [19,20]

1.2.2 Biomass application models

In future bio-based economies, the utilisation of biomass is not limited to the food sector and includes production of bio-energy, bio-fuels, bio-based chemicals, and performance materials [2]. Two application platforms may be envisaged, a high temperature thermochemical platform and a low temperature platform (Fig. 3). Both platforms convert biomass to heat and power, transportation fuels, bio-based chemicals and bio-based performance chemicals. A short overview of the platforms and products derived thereof will be given in the following.

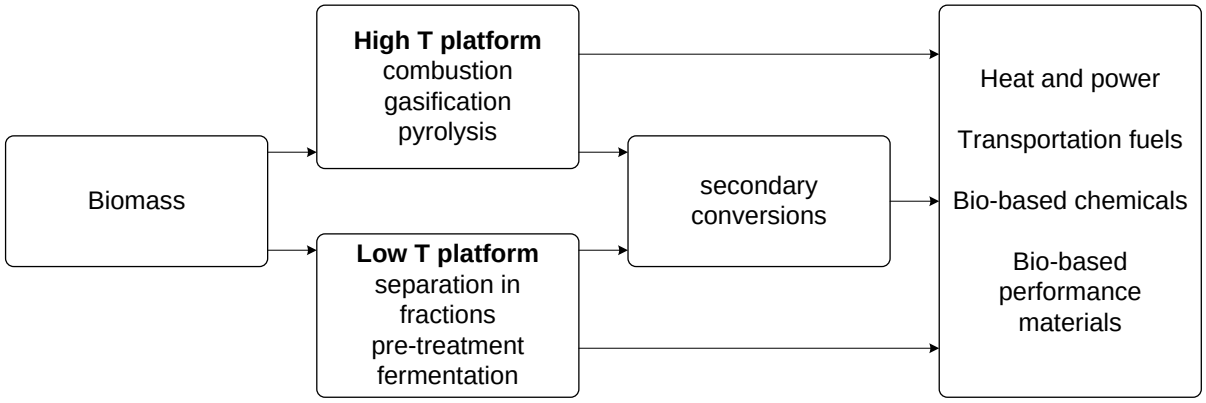


Fig. 3 Biomass conversion platforms

1.2.3 Bio-energy

Combustion of biomass to energy and heat is a very old process. Actually before 1850, biomass was the sole source for energy and heat generation. Recently, the use of biomass for power generation has gained renewed interest, particularly in the form of co-firing in power plants. Co-firing in coal-based power plants has been applied in the Netherlands, examples are the Amer (Essent), Maasvlakte (E.On Benelux), Gelderland (Electrabel), and Buggenum (Nuon) plants [21]. A compilation of global activities in the field of biomass co-firing is given in ref 22.

The utilisation of biomass for energy generation may, besides direct combustion, also be performed using gasification or fast pyrolysis. Gasification is performed at temperatures between of 750-1500 ^{o}C to produce flammable gas mixtures, known as synthesis gas ("syngas"), consisting of CO, H_2, CO_2, methane, nitrogen, and smaller quantities of higher hydrocarbons [23]. These product gases not only can be used for heat and power generation, but also as a feedstock for further chemical reactions or fermentations to produce liquid fuels and chemicals.

Fast pyrolysis is the rapid thermal decomposition of biomass/organic compounds at temperatures between 400-600 ^{o}C in the absence of oxygen to produce liquids, gases, and char [24]. The liquid product is known as "bio-oil" or "pyrolysis oil", and is a complex mixture of low and medium molecular weight sugars, aldehydes, furans, phenolic compounds, and (aromatic) acids.

1.2.4 Bio-fuels

Currently, bio-fuels from biomass are mainly produced from plant oils and the starch fraction of biomass. The first use of plant oils for transportation fuels was reported by Rudolf Diesel in 1912 and involved the use of peanut oil as a fuel for diesel engines [25]. About 25 years ago, the use of plant oils became important as raw material for the production of fatty acid methyl esters (bio-diesel) by a *trans*-esterification reaction [26,27].

Starch based biomass is an important feedstock for the production of bio-ethanol by fermentation. A well-known example is the production of bio-ethanol from sugarcane, an existing commodity in Brasil. Both bio-diesel and bio-ethanol from starch sources are known as first generation bio-fuels [2,28]. The main disadvantage of both fuels is direct or indirect competition with food products and as such the use of such first generation biofuels has raised ethical questions.

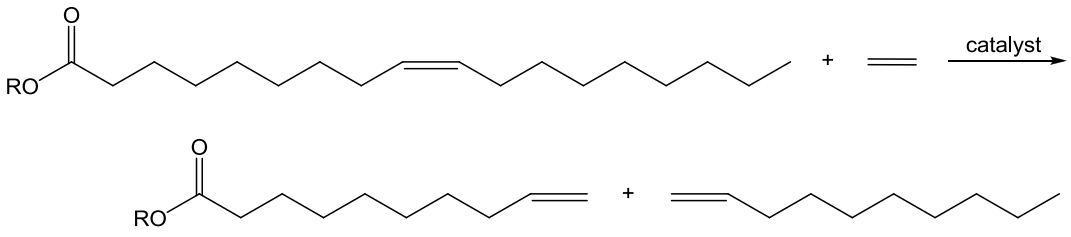
Second generation bio-fuels are produced from non-food feedstocks, for example cellulose, non-edible oils, and waste biomass [29-36]. Examples are bio-ethanol from lignocellulosic biomass and upgraded pyrolysis oils [37]. These processes are in the development phase and expected to become major bio-fuels in the coming decade. Third generation bio-fuels are from non-edible feedstocks which avoid food, fuel, and land use issues, an example is bio-diesel from marine biomass (algae) [27].

1.2.5 Bio-based chemicals

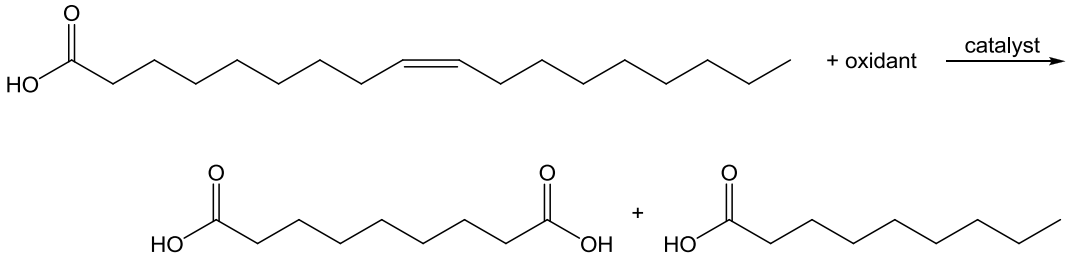
The current global chemical industry is heavily based on fossil feeds like oil and oil-derived fractions (naphta) and natural gas. However, about 10% of the input comes from biomass in the form of plant oils (oleochemical industry) and starch [38]. Bio-based chemicals are defined as (intermediate) chemicals derived from biomass through extraction (and further processing) and purification. The chemicals have a low molecular weight (typically less than 300 Da), and are usually sold with a certain purity [39]. Examples of bio-based chemicals are biomass derived fatty acids, other acids like levulinic-, succinic- and acetic acid, hydroxymethylfurfural, glycerol, phenols, and furfural [5].

1.2.5.1 Plant oils

Currently, over 100 million tonnes of oils and fats are produced annually. About 14% is used for the production of chemicals. Plant oils are not used as such but converted to basic oleochemicals, such as fatty acids (52%), fatty acids methyl esters (11%), fatty amines (9%), and fatty alcohols (25%) [40]. These are the building blocks for the production of bio-based performance materials such as surfactants, paints, and lubricants by further chemical modifications [41]. New, upcoming activities with large market potential are the production of olefins (eq. 1) [42,43], di-carboxylic acids (eq. 2) [44], and biohydrocarbons (eq. 3) (32,34,45). Other interesting bio-based chemicals can also be produced from the glycerol byproduct [3].



(eq. 1)



(eq. 2)

Fatty acids (esters) + H_2 $\xrightarrow{\text{catalyst}}$ **(C15 + C16) alkanes** + CO + CO_2 + CH_4 + H_2O + .. (eq. 3)

1.2.5.2 Carbohydrates

The US Department of Energy recently published reports on interesting chemical building blocks from carbohydrates (Table 3). Chemical and biotechnological conversion routes were reviewed and ranked in terms of functionality, industrial viability, market, energy efficiency, and cost [46].

Table 3 Bio-based chemicals derived from carbohydrates

Data 2004 [3]	**Data 2010** [46]
1,4-diacids (succinic, fumaric, malic)	Succinic acid
2,5-furan dicarboxylic acid	Furanics
3-hydroxy propionic acid	Hydroxy propionic acid / aldehyde
Glycerol	Glycerol and derivatives
Sorbitol	Sorbitol
Xylitol/arabinitol	Xylitol
Levulinic acid	Levulinic acid
Aspartic acid	Biohydrocarbons
Glucaric acid	Lactic acid
Glutamic acid	Ethanol
Itaconic acid	-
3-hydroxybutyrolactone	-

Glycerol was included in the list as it is considered as “mini-sugar” [46] and is the by-product of the growing biodiesel industry which has a high application potential [3]. Other recent advancements in this field include the synthesis of [27,47,48,49]:

- (1-, 2- and *iso*-) bio-butanol from carbohydrates and woody biomass,
- bio-ethanol from cellulosic materials and syngas,
- bio-ethanol, bio-butanol, acetate, and butyrate by fermentation of syngas components, and
- ethers of 5-hydroxymethylfurfural.

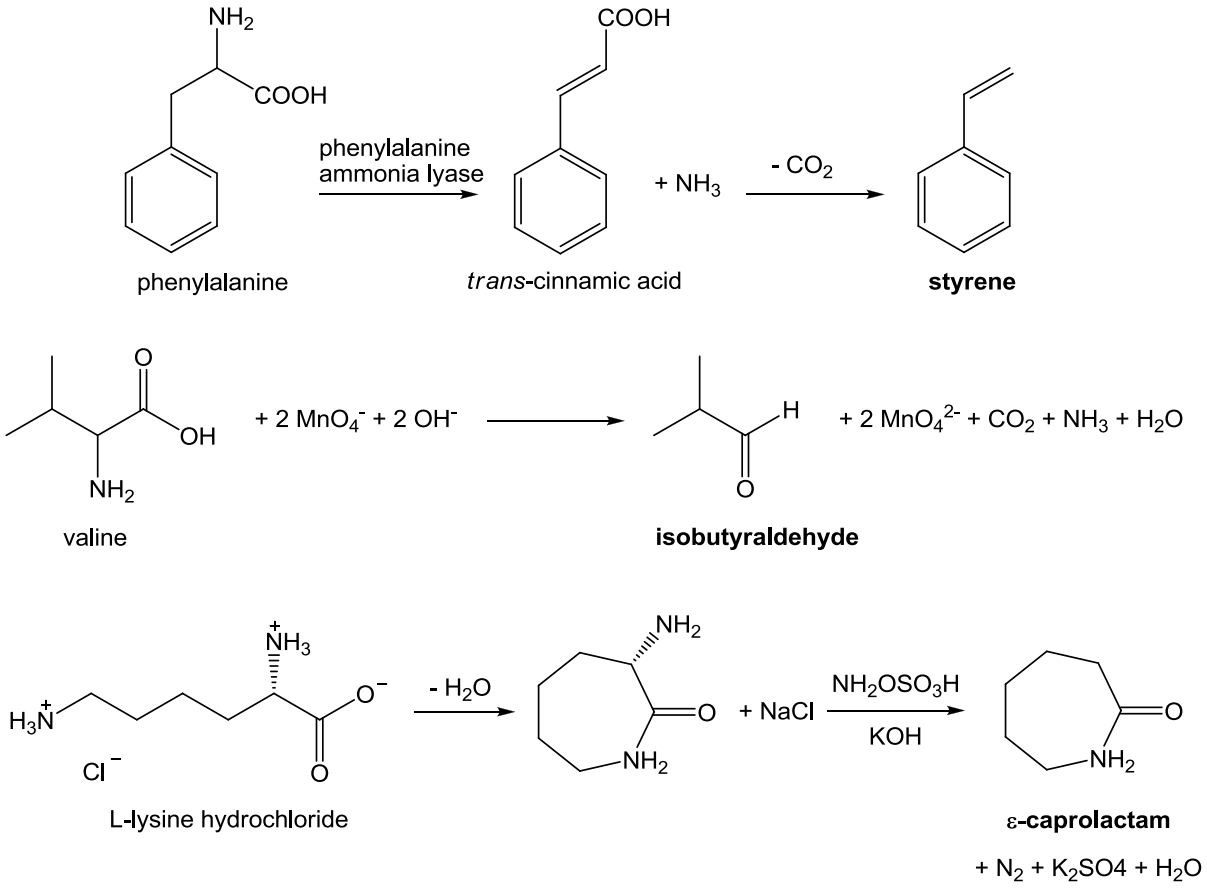
Bio-butanol is considered as a more suitable gasoline blend than bio-ethanol [50,51] and scale-up is actively pursued by several companies [48]. However, the relatively low yield and efficiency as well as relatively higher processing cost of bio-butanol compared to bio-ethanol are still challenging issues [50-52]. An interesting example of the integrated production of bio-fuels and bio-based chemicals from sugars is the co-production of bio-ethanol (or bio-butanol) and succinic acid [53].

1.2.5.3 Lignins

Several routes have been explored to obtain bio-based chemicals from lignin. An interesting example is the use of pyrolysis technology to breakdown the polymeric network into a range of aromatic compounds. Fast fluidised bed pyrolysis of different lignins at 400 ^{o}C gave up to 21 wt% (dry basis) of a phenolic fraction containing guaiacols, syringols, alkyl phenols, and catechols [54]. Some low molecular weight acids, aldehydes, and ketones, and gases like CO, CO_2, and CH_4 were formed as well. Anothere example involves catalytic hydrotreatment of lignin at 300 – 450 ^{o}C using hydrogen gas (100 – 200 bars) and heterogeneous metal catalysts [55,56].

1.2.5.4 Proteins

Proteins are long chain polyamides consisting of amino acids units [4]. Free amino acids may be obtained by protein hydrolyses using various techniques [57]. Amino acids have potential to be used for the production of existing chemical products from petroleum resources (e.g. styrene, isobutyraldehyde, and ε-caprolactam, see Scheme 1), as reviewed by Sanders [58].



Scheme 1 Examples of bio-based chemicals from amino acids [58]

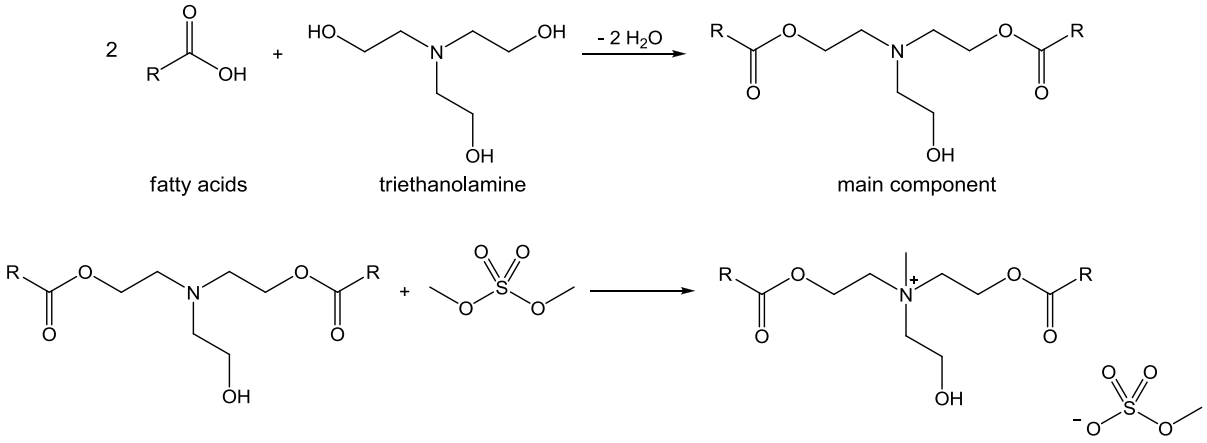
1.2.6 Bio-based performance materials

Bio-based performance materials are complex, formulated products of which the function is of prime importance and not the purity [59]. Examples are lubricants, inks, dyes and pigments, paints and varnishes, detergents and cleaners, industrial adhesives, biopolymers, and composite materials [5]. Similar to bio-based chemicals, bio-based performance materials may originate from various plant products, examples are plant oils, carbohydrates, lignin, as well as proteins.

1.2.6.1 Plant oils

Plant oil derivatives already find widespread applications in the fields of surfactants and bio-lubricants/hydraulic fluids [40]. A major advantage is their high biodegradability. This is particularly relevant when considering that surfactants are discarded entirely after use and end up in the environment, while the total loss for lubricants and hydraulic fluids during use are estimated at 50% and 70-80%, respectively [60].

The performance requirements for both application fields differ and as a result different plant oil feeds are used. For example, lauric oils from e.g. palm-kernel oil and coconut oil as well as stearin from palm oil are the dominant feedstock for the surfactant market. In these applications, the oils are initially converted into fatty acids or fatty alcohols. A well known example is the triethanolamine (TEA)-based esterquats (Scheme 2) [61], primary ingredients in European fabric softeners [62]. The surfactant contains branched structures which show enhanced performance compared to their linear counterparts, such as lower viscosity, ease of handling, and better hard water tolerance [63].



Scheme 2 Esterquats from fatty acids [61]

A range of plant oils are used as lubricant base fluids, the actual choice depending on lubrications purpose. Native plant oils are suited and limited in applications where total loss is unavoidable, for example as lubricants for chainsaws and concrete mould release oils, as well as applications involving very low thermal stress [60]. Examples of plant oils used in these applications are palm (Castrol

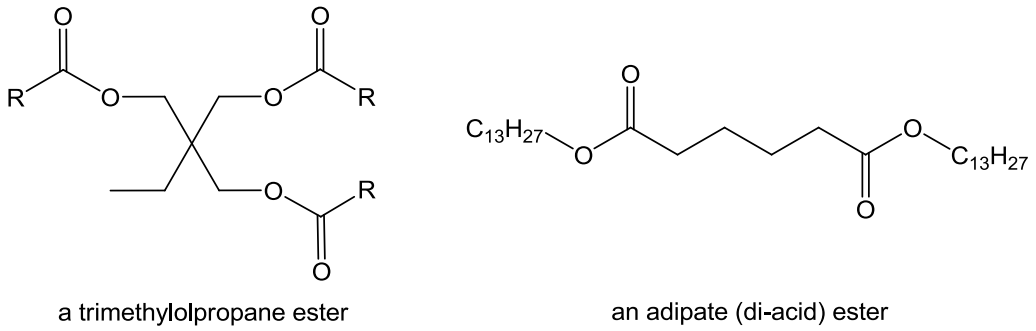
Palmtec 2T and 4T), soybean, canola, low erucic rapeseed, high oleic sunflower, cotton, and castor oil [60,64-66]. For many applications though, plant oils are modified to meet specific requirements. Some well known commercial brands are, among others, Bioadd 751 (Shrieve), Dehylube 1000 (Cognis), Radiagreen SL (Oleon), and Drewmulse (Stepan) [67]. The advantages and disadvantages of plant oil-derived lubricants are provided in Table 4.

Table 4 Advantages and disadvantages of plant oils-derived lubricants [60]:

Advantages	**Disadvantages**
excellent tribological properties (ester groups adhere well to metal surfaces)	lower thermal stability compared to petroleum-based lubricants
lower friction coefficients than petroleum-based lubricants	poor hydrolytic stability
lower volatility, typically 20% less than petroleum-based lubricants	poor oxidative stability
higher viscosity index	poor low temperature behaviour
excellent biodegradability	
high flash points	
low water pollution classification	

The commercial plant oil derived lubricants consist of two major compound classes: polyol-esters and di-acid esters (Fig. 4) [60,68]. Both of them are biodegradable and have a low toxicity. Polyols are used to replace the glycerol chain in plant oils with the incentive to improve the stability towards hydrolysis and thermal degradation [60]. Common polyols are trimethylolpropane [69], neopentyl glycol, and pentaerythritol [70,71]. Some of the esters are used in extreme conditions, such as in jet engines or in arctic conditions [62]. Fatty acids used in the preparation of these compounds are oleic, and C5-C9 carboxylic acids [60].

The di-acid esters, are prepared from di-carboxylic acids derived from plant oils, such as azelaic acid, as well as from petroleum sources, such as adipic acid [60]. The alcohols are primarily branched alcohols, mainly from petroleum sources. Some relevant physical properties of ingredients in plant oil derived lubricants and a comparison with petroleum derived counterparts are given in Table 5.



a trimethylolpropane ester

an adipate (di-acid) ester

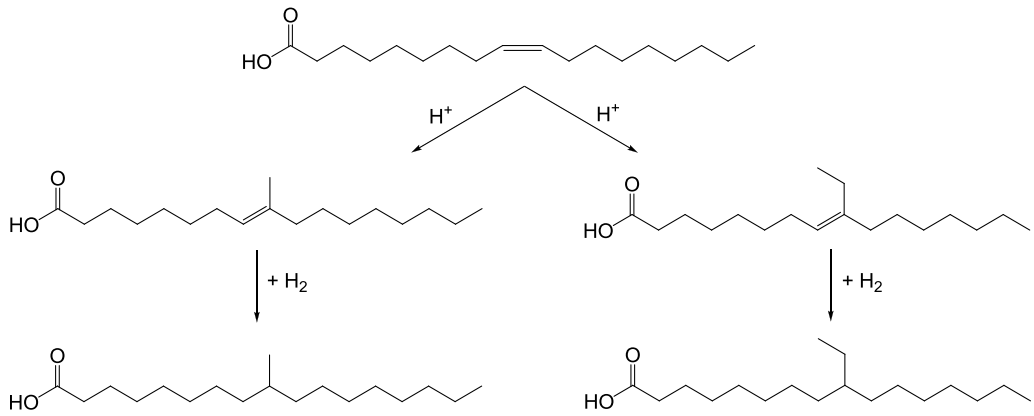
Fig. 4 Example of two major classes of lubricants derived from plant oils [68]. R=remaining fatty acid chains

Table 5 Physical properties of plant oils-derived and petroleum-derived lubricants [60,68]

	Plant oils-based			Petroleum-based	
	Rapeseed oil	*Polyols*	*Di-esters*	*Mineral oil (150N)*	*Phthalates*
Viscosity at 40 °C (cSt)	33	14 to 35	6 to 46	ISO 32	29 to 94
Pour points (°C)	-21	-60 to -9	-70 to -40	-12	-50 to -30
Flash point (°C)	n.a.	250 to 310	200 to 260	n.a.	200 to 270
Oxidative stability	moderate	moderate to good	moderate to good	excellent	very good
% biodegradability	100	90 to 100	75 to 100	15	46 to 88

The oxidative stability of plant oils is determined by the amount and type of carbon-carbon double bonds. The best solution to improve the oxidation stability is a reduction of the amount of C-C double bonds, for instance by hydrogenation [60]. However, fully hydrogenated plant oils are solids at room temperature, and this limits application. A solution is the introduction of branched structure elements in the product [72-76]. In general, the presence of branches hinders a regular alignment and close packing of the fatty acid chains [77]. This results in lower melting points, which is advantageous compared to the non-branched analogues. Furthermore, branched fatty acids also have a positive effect on the cold-flow properties of bio-diesel [78]. The use of branched fatty acids in cosmetic products has been reported as well [79].

Branched-chain fatty acids are accessible by a vast number of chemical and enzymatic reactions. Some are commercially available as by-products from dimer acid production from unsaturated fatty acids. Versatile synthetic routes include the ring opening of commercially available epoxidised plant oil, such as epoxidised soybean oil [80], *trans*-esterification with branched alcohols [81], and isomerisation of oleic acid followed by hydrogenation [63], see Scheme 3 for details. The latter branched products show excellent low temperature behaviour, have a low viscosity, and high flash point [60].



Scheme 3 Production of branched chain fatty acids by isomerisation – hydrogenation

1.2.6.2 Carbohydrates

Modified starches are important bio-based performance materials and have improved product properties compared to native starch (lower hydrophilicity, better gelatinisation properties and lower viscosity in water) [82]. Modification of starch can be performed by physical, chemical, and enzymatic methodology, or combinations thereof [82].

Starch esters and ethers are two important classes of commercial starch-based performance materials with applications as thickeners, suspension agents, protective colloids, and building materials [83]. Bio-degradable packaging materials from starch have also received considerable attention in the last decade [84,82,85]. A commercial example is BIOPAC [86]. Starch ethers, produced commercially by AVEBE, are used as building materials [87].

Cellulose may also be modified and commercial examples are cellulose ethers/esters and cellulose based nanomaterials and composites. Cellulose ethers and esters find applications as films and fiber materials, coatings, oil-well drilling muds, paints, detergents, and adhesives [88,89]. Meanwhile, cellulose nanomaterials and composites are used for fiber reinforcement, packaging materials and optically transparent nanocomposites for electronic devices [90].

1.2.6.3 Lignins

The use of lignin for the production of bio-based performance materials is limited to date, though some examples are available for lignins from the paper and pulp industry (lignosulfonates and kraft lignins) [91]. Lignosulfonates are produced by partial cleavage of lignin by hydrolysis into smaller fragments followed by introduction of sulfonic acid group. Lignosulfonates have surfactant-like properties and are used for emulsification and dispersion processes. Minor applications include the use as road dust suppressant, as food pellet binders, and as animal feed additive. Table 6 summarises the major applications of lignosulfonates.

Table 6 Examples of lignosulfonate applications as performance materials [91]

Crude spent liquor lignosulfonates	Refined lignosulfonates
Feed and pellet binders	Oil well drilling fluids
Feed molasses extenders	Dye and pigment dispersants
Dust suppression and road stabilisation	Tanning agent
Agricultural dispersants and emulsifiers	Gypsum board manufacture
	Cement manufacture
	Refractory clays and ceramics
	Phenolic resins
	Lead acid storage battery plates

Kraft lignins are obtained from the kraft pulping process, which involves the delignification of wood by thiolysis using a combination of sodium hydroxide and sodium sulfide [91]. Kraft lignins may be used in rubber formulations, as activated carbon, a carbon black substitutes, and phenolic resin components.

In the last decade, considerable research activities have been performed on the modification/application of lignin for performance products and particularly to act as a binder and to improve mechanical strength of the matrix [92]. Both enzymatic and chemical routes, for example by partial oxidation [92-94] or (grafting) polymerisation [94,95], combined with mechanical techniques are common practice leading to a large variety of products such as artificial plastics and particle boards.

1.2.6.4 Proteins

Proteins are used in many daily life products, examples are the use as adhesives, coatings, and surfactants [96]. Some important product properties of the proteins that determine its potential application are solubility at different pH, emulsifying, foaming, film forming, and adhesive properties [97]. Proteins with good emulsifying properties are used as surfactants. All properties are highly depending on the protein source and the method of isolation [98-100].

1.3 The biorefinery concept

1.3.1 General

The biorefinery concept is a powerful tool in the bio-based economy. The National Renewable Energy Laboratory (NREL), US Department of Energy defines a biorefinery as follows: "*A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass*." [2]. Within this concept, the overall processes should be performed with a minimum loss of energy and mass to maximise the overall value of the production chain. It consists of an efficient fractionation of the biomass into various value-added products and energy using physical separation processes in combination with (bio-) chemical and thermochemical conversion steps. In this respect, the biorefinery concept is analogous to today's crude oil refineries, which produce multiple products in a material- and energy efficient manner.

An example of an existing biorefinery industry is the starch-based biorefinery operated by Roquette [101]. It involves an integrated biorefinery for corn, wheat, potato, and pea to produce a range of bio-based products and bio-based performance materials. The Roquette biorefinery scheme is presented at Fig. 5.

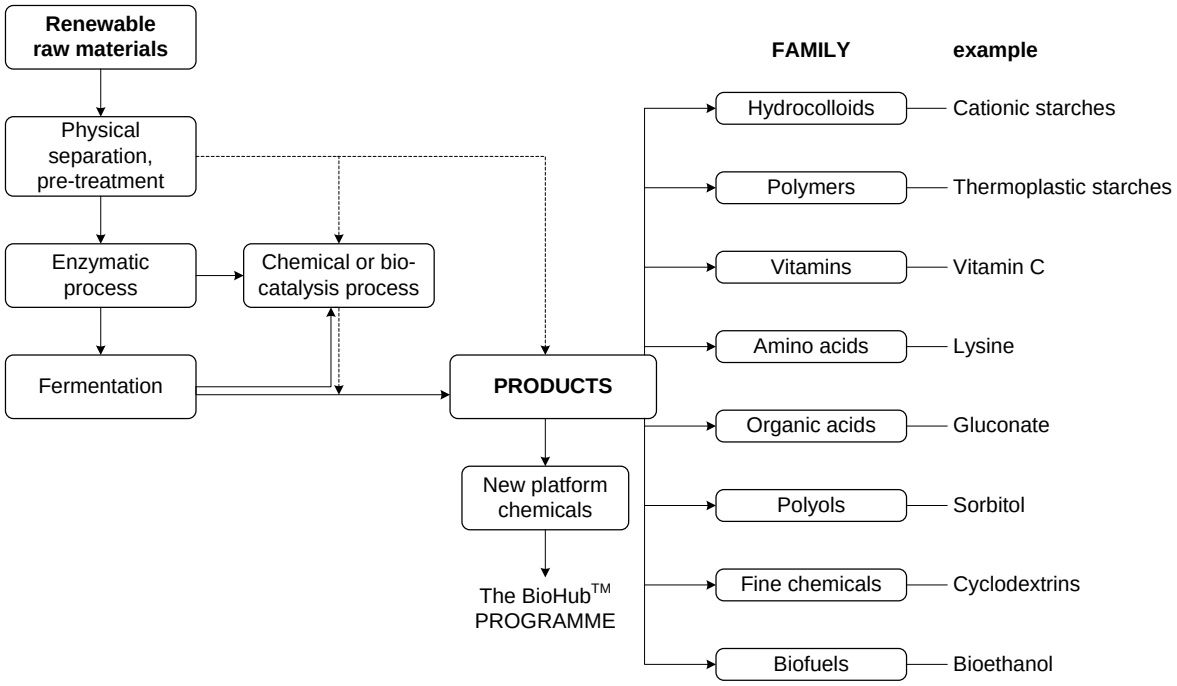


Fig. 5 Starch-based biorefinery by Roquette [102]

1.3.2 Oil-bearing plant biorefineries

The biorefinery concept is also applicable for plants and trees producing oil bearing seeds. In contrast to common practice, the objective is to achieve full valorisation of the plant/tree and the focus is not only on the product oil. A schematic overview of the concept is given in Fig 6. It involves separation of the various valuable components like plant oils, proteins, starch-cellulose and lignin. In the next step, these components are converted to a range of end products.

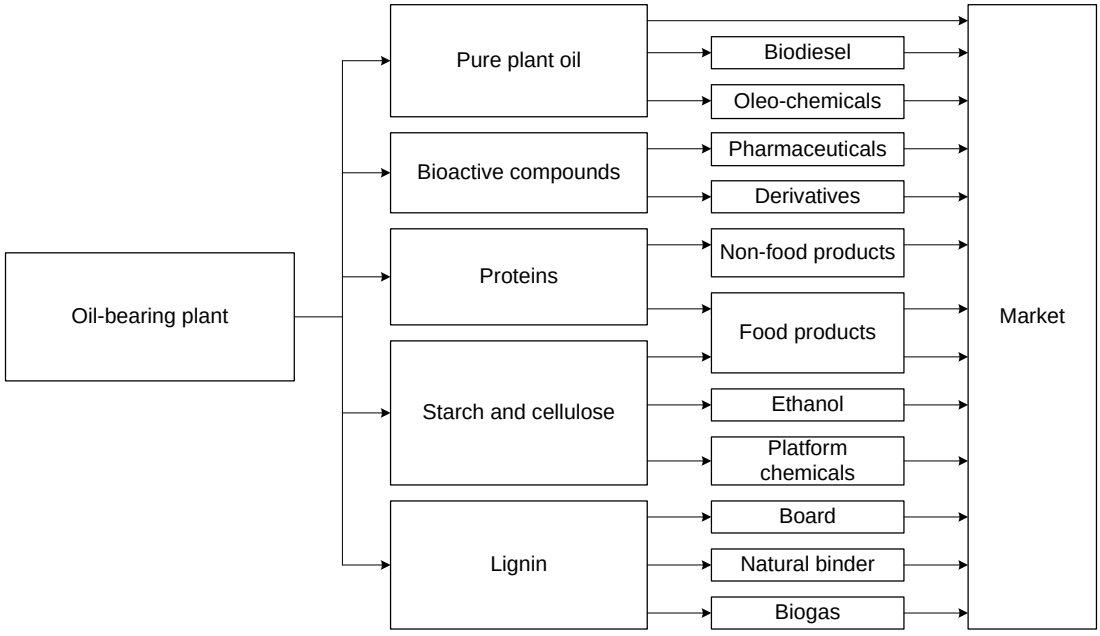


Fig. 6 Biorefinery concept for oil-bearing plant

1.4 Indonesian plant oil resources

Indonesia is rich in plant oil resources and at least 54 oil-bearing plants have been identified (see Table 7). Palm is the country's number one plant oil with an annual production of 3-6 tonnes oil/ha [103]. Next to palm and palm kernel oil, soybean, coconut, and castor are also important [105].

Table 7 List of plant oil resources in Indonesia [104,105]

No	Indonesian name	English name	Latin name	Source of oil	Oil content (dry basis) [wt%]	E / NE[a)]
1	Jarak kaliki	Castor	*Ricinus communis*	Seed	45 – 50	NE
2	Jarak pagar	Jatropha	*Jatropha curcas*	Seed kernel	40 – 60	NE
3	Kacang kedelai	Soybean	*Glycine max*			E
4	Kacang suuk	Peanut	*Arachis hypogea*	Seed	35 – 55	E
5	Kapok/randu	Kapok	*Ceiba pentandra*	Seed	24 – 40	NE
6	Karet	Rubber	*Hevea brasiliensis*	Seed	40 – 50	NE
7	Kecipir	Winged bean	*Psophocarpus tetrag.*	Seed	15 – 20	E
8	Kelapa	Coconut	*Cocos nucifera*	Mesocarp	60 – 70	E
9	Kelor	Moringa	*Moringa oleifera*	Seed	30 – 49	E
10	Kemiri	Candlenut	*Aleurites moluccana*	Seed kernel	57 – 69	NE
11	Kusambi	Kusambi	*Sleichera trijuga*	Kernel	55 – 70	NE
12	Nimba	Neem	*Azadirachta indica*	Kernel	40 – 50	NE
13	Saga utan	Red sandalwood	*Adenanthera pavonina*	Seed kernel	14 – 28	E
14	Sawit	Palm	*Elais guineensis*	Pulp + mesocarp	45 – 70 + 46 - 54	E
15	Akar kepayang	Kapayang	*Hodgsonia macrocarpa*	Seed	~ 65	E
16	Alpukat	Avocado	*Persea gratissima*	Mesocarp	40 – 80	E
17	Cokelat	Chocolate	*Theobroma cacao*	Seed	54 – 58	E
18	Getap pait	Niepa bark	*Samadera indica*	Seed	~ 35	NE
19	Kepoh	Java olive	*Sterculia foetida*	Seed kernel	45 – 55	NE
20	Ketiau	Katiau flowerbuds	*Madhuca mottleyana*	Seed kernel	50 – 57	E
21	Malapari	Karanja	*Pongamia pinnata*	Seed	27 – 39	NE
22	Nyamplung	Polanga	*Callophyllum inophyllum*	Seed kernel	40 – 73	NE
23	Randu alas/agung	Cotton tree	*Bombax malabaricum*	Seed	18 – 26	NE
24	Seminai	Bitis	*Madhuca utilis*	Seed kernel	50 – 57	E

25	Siur(-siur)	n.a.[b)]	*Xanthophyllum lanceatum*	Seed	35 – 40	E
26	Meranti merah, tengkawang tungkul	Brown illipe nuts, red meranti	*Shorea stenoptera*	Seed kernel	45 – 70	E
27	Tengkawang terindak	Balau	*Isoptera borneensis*	Seed kernel	45 – 70	E
28	Wijen	Sesame	*Sesamum orientale*	Seed	45 – 55	E
29	Bidaro	Yellow plum, sea lemon	*Ximenia americana*	Seed kernel	49 – 61	NE
30	Bintaro	Sea mango	*Cerbera manghas /odollam*	Seed	43 – 64	NE
31	Bulangan	Asian bushbeech	*Gmelina asiatica*	Seed	n.a.[b)]	NE
32	Cerakin/ kroton	Purging croton	*Croton tiglium*	Seed kernel	50 – 60	NE
33	Kampis	n.a.[b)]	*Hernandia peltata*	Seed	n.a.[b)]	NE
34	Kemiri cina	Lumbang tree	*Aleurites trisperma*	Seed kernel	n.a.[b)]	NE
35	Labu merah	Squash, pumpkin	*Cucurbita moschata*	Seed	35 – 38	E
36	Mayang batu	n.a.[b)]	*Madhuca cuneata*	Seed kernel	45 – 55	E
37	Nagasari (gede)	Ceylon ironwood	*Mesua ferrea*	Seed	35 – 50	NE
38	Pepaya	Papaya	*Carica papaya*	Seed	20 – 25	E
39	Pulasan	Pulasan	*Nephelium mutabile*	Seed kernel	62 – 72	E
40	Rambutan	Rambutan	*Nephelium lappaceum*	Seed kernel	37 – 43	E
41	Sirsak	Soursop	*Annona muricata*	Seed kernel	20 – 30	NE
42	Srikaya	Custard-apple	*Annona squamosa*	Seed	15 – 20	NE
43	Kenaf	Deccan hemp	*Hibiscus cannabinus*	Seed	18 – 20	NE
44	Kopi arab (Okra)	Okra, lady's fingers	*Hibiscus esculentus*	Seed	16 – 22	NE
45	Rosela	Roselle	*Hibiscus sabdariffa*	Seed	~ 17	NE
46	Kayu manis	Cinnamon	*Cinnamomum burmanni*	Seed	~ 30	E
47	Padi	Rice	*Oryza sativa*	Bran	~ 20	E
48	Jagung	Corn	*Zea mays*	Germ	~ 33	E
49	Tangkalak	Bombi	*Litsea sebifera*	Seed	~ 35	E
50	n.a.	n.a.	*Taractogenos kurzii*	Seed kernel	48 – 55	NE

51	Kursani	Iron weed	*Vernonia anthelmintica*	Seed	~ 19	NE
52	Tembakau	Tobacco	*Nicotiana tabacum*	Seed	36 - 41	NE
53	Tomat	Tomato	*Solanum lycopersicum*	Seed	32 – 37	NE
54	Jojoba	Jojoba	*Simmondsia chinensis*	Seed	45 – 55	NE

a) E = edible; NE = non-edible; b) n.a. = not available or unknown

The food versus fuel discussion has triggered the introduction of new plant oils which are non-edible and as such do not compete with the food sector. One of the interesting possibilities in this category is *Jatropha curcas* oil (JO), a non-edible oil extracted from the *Jatropha curcas* Linnaeus (JCL) shrub/tree.

Indonesia also produces plant oils having highly reactive functional groups, an example is the oil from the *Sterculia foetida* tree (STO). STO contains cyclopropene rings which allow for a range of chemical modification reactions. About 70% of the fatty acids in STO contain cyclopropene units, which is the highest among all other plant oils [106].

Both the valorisation of the *Jatropha* curcas L and *Sterculia foetida* L using the biorefinery concept will be discussed in the following sections.

1.4.1 Oil plant biorefineries: the *Jatropha curcas* Linnaeus (JCL) case

JCL, also known as physic nut [107] or purging nut [108], is a tropical, drought-resistant shrub/tree belonging to the genus Euphorbiaceae, and is cultivated in Central and South America, South-east Asia, India, and Africa [109]. The Jatropha name itself was derived from the Greek “jatrós” (doctor) and “trophé” (food) [110]. It has two genotypes, a toxic and non-toxic one, the latter is found in Mexico only [110]. The tree has excellent adaptation capacity to various soil conditions. Traditionally, the trees are used for erosion control as well as fencing, to protect plantations from wild animals [109].

Fig. 7 Parts of *Jatropha curcas* tree [113]

The tree can live up to 50 years [111]. Typically, the tree grows to 3-4 m in height [112], but under favourable conditions it can reach up to 12 m [110]. The fruit contains usually 2-3 seeds, each with a weight of about 600-700 mg [107]. The seeds consist of a kernel (60 wt%) and shell (40 wt%) [108]. The oil content in the seed ranges from 30-40 wt%, which corresponds to 45-55 wt% based on the seed kernel [107]. The chemical composition of the JCL seeds from a number of varieties is presented in Table 8.

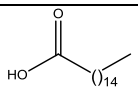
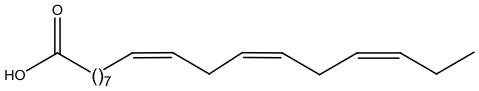
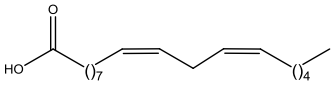
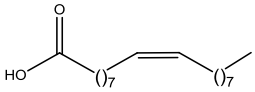
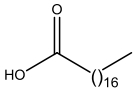
Table 8 Chemical composition of kernel, shell, and husk of some *Jatropha curcas* varieties [108]

Item	**Variety**					
	Cape Verde		*Nicaragua*		*Non-toxic Mexico*	
	Kernel	*Shell*	*Kernel*	*Shell*	*Kernel*	*Shell*
Dry matter	96.6	90.3	96.9	90.4	94.2	89.8
Components (wt%, dry basis)						
Crude protein	22.2	4.3	25.6	4.5	27.2	4.4
Lipid	57.8	0.7	56.8	1.4	58.5	0.5
Ash	3.6	6.0	3.6	6.1	4.3	2.8
Neutral detergent fiber	3.8	83.9	3.5	85.8	3.8	89.4
Acid detergent fiber	3.0	74.6	3.0	75.6	2.4	78.3
Acid detergent lignin	0.2	45.1	0.1	47.5	0.0	45.6

The main constituents in the seed kernel are the lipid/oil, while fibers are the major component in the seed shell.

The first commercial applications of JCL oil are as a feed for the manufacture of soap and the use as a lamp oil [109]. The fatty acid composition of the oil (JO) shows some similarities with soybean oil (SO) (see Table 9). In the last decade, interest in JO oil was mainly for biodiesel production.

Table 9 Fatty acids composition of Jatropha and soybean oil (in wt%)

Fatty acids			**JO** [109]	**SO** [114]
Palmitic acid	C16:0		14.1-15.3	11
Linolenic acid	C18:3		0-0.3	8
Linoleic acid	C18:2		29.0-44.2	54
Oleic acid	C18:1		34.4-45.8	23
Stearic acid	C18:0		3.7-9.8	4
Total unsaturated fatty acids fraction			**63.4-91.6**	**85**

Valorisation of *Jatropha curcas* L. plant using the biorefinery concept

An integrated concept for the valorisation of the *Jatropha curcas* L. plant was proposed by Gübitz [109] and is presented in Fig. 8. According to this scheme, all parts of JCL have possibilities to be used for interesting applications. Table 10 summarises possible outlets of all plant parts, including uses as bio-based products or bio-based performance materials, and is an extension of the work of Gübitz.

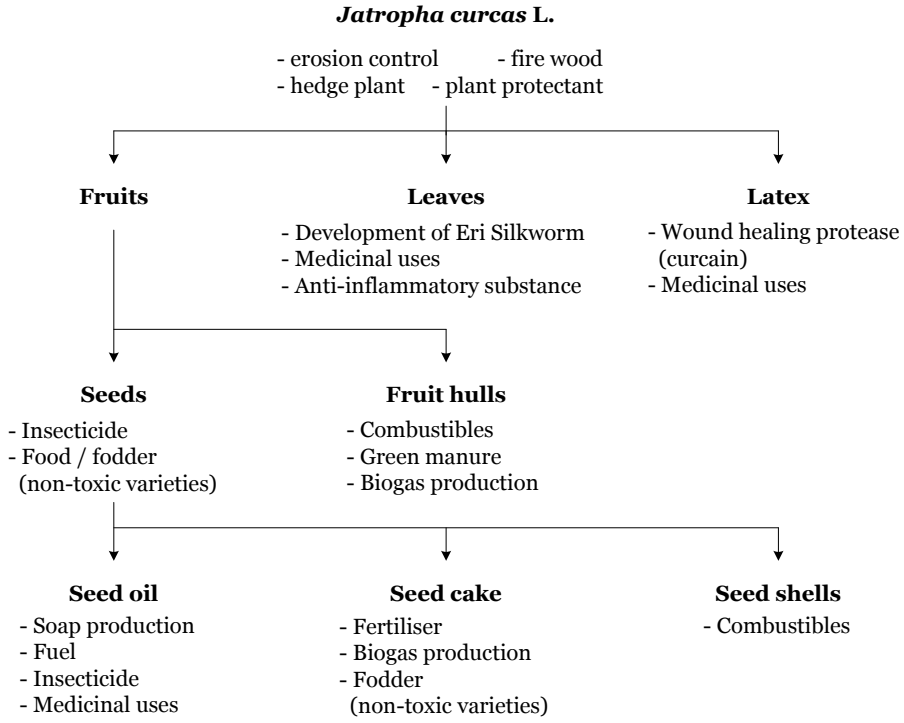


Fig. 8 Valorisation of *Jatropha curcas* L. plant using biorefinery concept [109]

Table 10 Literature reports on the valorisation of *Jatropha curcas* L. plant

Parts	Potential applications	References
Oil	bio-diesel fuel	115
	novel renewable-diesel fuel	33, 34, 116, 117
	building block chemical	118,119
	polymer	120,121
Oil aqueous-extract	pesticide	109
Pressed-cake and leaves proteins	animal feed	122
	adhesives	123
	emulsifier	97
	fertiliser	109
	raw material for biogas production	124
Seed, leaves, bark, latex, twig/stem	medicinal uses	125
Seed shell	fiber boards	126
	low grade biofuel	127,128

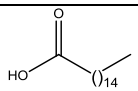
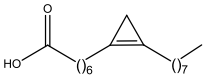
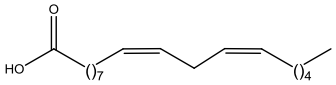
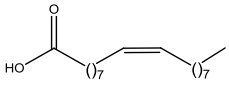
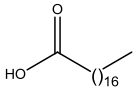
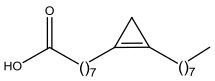
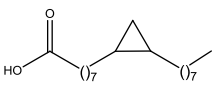
1.4.2 Oil plant biorefineries: the *Sterculia foetida* Linnaeus (STL) case

STL, also known as Java olive, hazel sterculia, or wild almond tree, is a tropical tree that is natively widespread from East Afrika, Myanmar, Srilanka, Borneo, Java, Sumatra, Indo-China, to North Australia [129,130]. STL is a large, straight, evergreen tree growing up to 40 m in height and 15 m in girth [129]. The name originates from the Latin word "stercus", meaning "manure", and the malodorous nature of the tree is emphasised by its species name, "foetida", meaning "stinking" [129].

The seed kernel contains 53-55 wt% of a pale yellow oil which polymerises rapidly at 240 – 250 °C and even to some extent at low temperatures [130]. The defatted press cake contains about 40 wt% of crude protein and 44.4 wt% of carbohydrates [131]. The fatty acid composition of STO is presented in Table 11.

Fig. 9 Parts of *Sterculia foetida* tree [132]

Table 11 Typical fatty acid composition of *Sterculia foetida* L. oil (STO)

Fatty acids			**wt%** [133]
Palmitic acid	C16:0		20.0
Malvalic acid	C18:CE		11.4
Linoleic acid	C18:2		4.12
Oleic acid	C18:1		8.3
Stearic acid	C18:0		0.54
Sterculic acid	C19:CE		55.7
Dihydrosterculic acid	C19:CA		-
Total cyclopropenoid fatty acids fraction			**67.1**

Valorisation of *Sterculia foetida* L. plant using the biorefinery concept

The last decade, a number of reports on the valorisation of *Sterculia foetida* L. plant have appeared in the open literature. However, the full spectrum of promising products has not been described as comprehensively as for the Jatropha case. Research articles have been devoted to the characterisation of the plant, utilisation of the seed oil as well as other parts of the plant. Table 12 summarises available literature reports on the valorisation of STL plant.

Table 12 Literature reports on the valorisation of *Sterculia foetida* L. plant

Parts	Potential applications	Reference
Oil	Biodiesel fuel	134
	Biolubricant	135
Pressed-cake proteins	Baking products	131
Gum	Controlled release materials	136
Seed extracts	Insecticidal	137,138
Leaves	Pharmaceuticals	139-141

1.5 This thesis

This thesis describes exploratory studies on the valorisation of Indonesian plant oil resources and particularly JCL and STL. Valorisation studies include plant oil modifications as well as conversion of the remaining lignocellulosic fraction to bio-based chemicals, as schematically given in Fig. 10.

In **Chapter 2**, the synthesis and properties of highly branched JO derivatives are described and discussed. The synthetic strategy includes epoxidation and dihydroxylation followed by esterification to introduce branches in the fatty acid chain. Relevant product properties of the branched products were determined and the effect of the stereochemical configuration of the branches on the cold-flow properties was studied.

In **Chapter 3**, the synthesis of branched JO ester derivatives by a *trans* esterification-alkoxylation reaction with various alcohols and metal triflate catalysts is described. Initial studies were performed with methyl oleate and oleic acid as model compounds. The best catalyst was selected for further studies using JO. Relevant product properties of the branched product were determined and related to the molecular structure.

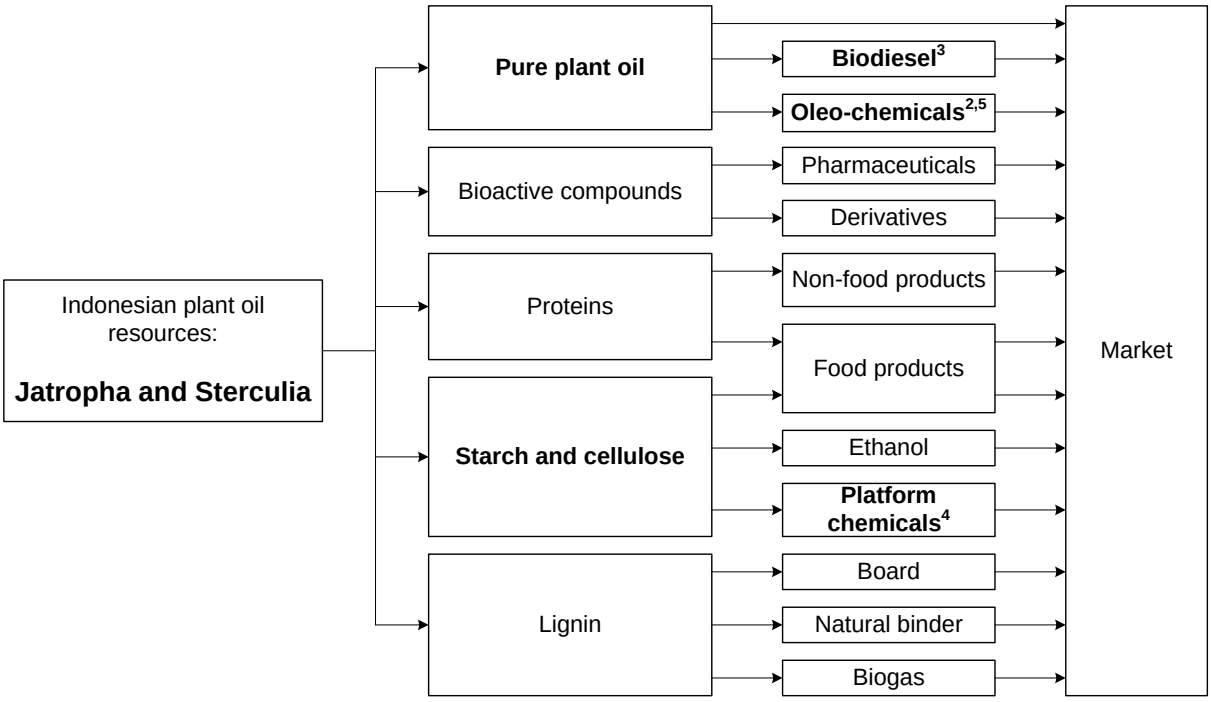


Fig. 10 Valorisation of Indonesian plant oil resources using biorefinery concept (superscripts = the corresponding chapter numbers in this thesis)

In **Chapter 4**, studies on JCL seed shell valorisation are described. The shell is rich in carbohydrates and as such could be an attractive feed for the synthesis of interesting bio-based chemicals like succinic acid. Initially, exploratory catalyst screening studies on the catalytic oxidation of levulinic acid to succinic acid at mild conditions were performed with either hydrogen peroxide or oxygen as the oxidant. In the final stage, JCL seed shells were used as starting material to assess their potential as a feed for succinic acid synthesis.

Chapter 5 describes an exploratory study on the synthesis of branched ester derivatives of STO using a range of synthetic modification strategies for cyclopropene rings, including Diels-Alder, olefin metathesis, oxidation, as well as rearrangement reactions. Relevant product properties were determined and will be discussed.

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Chapter 2

Synthesis and properties of highly branched *Jatropha curcas* L. oil derivatives

Summary

The synthesis and properties of a number of novel branched *Jatropha curcas* L. oil (JO) derivatives containing vicinal di-ester units in the fatty acid chains are reported. Both the length (acetyl vs. hexanoyl) and the stereochemistry of the vicinal di-ester units (*cis* vs. *trans*) were varied. The compounds were prepared by two different synthetic approaches using catalytic chemistry. The first approach involves epoxidation of JO using a Sharpless epoxidation with methyltrioxorhenium as the catalyst to give epoxidised JO (**1**), followed by an esterification reaction with the corresponding anhydrides using ammonium-12-molybdophosphate (AMP) as catalyst to give *trans*- di-esters of JO (**4a, 4b**). The second approach is based on the dihydroxylation of JO using either the Prilezhaev method, resulting in *trans*-diols of JO (**2**), or the Upjohn method using osmium tetroxide as catalyst to give *cis*-diols of JO (**3**). In subsequent steps, the diols were esterified with acetic- or hexanoic anhydride using dimethylaminopyridine as catalyst to produce the corresponding *trans*- and *cis*- di-esters of JO (**5a, 5b, 6**). The best cold flow properties (lowest pour- and cloud point, crystallisation and melting temperature) were obtained for JO with hexanoyl branches in a *trans* orientation (**5b**, pour point of -14 ^{o}C, melting point of -5 ^{o}C, and crystallisation temperature of -25 ^{o}C) and these values are considerably better than for the JO source.

Keywords: branched derivatives, epoxidation, dihydroxylation, esterification, *Jatropha curcas* L. oil

2.1 Introduction

The last decade, *Jatropha curcas* L. oil (JO) has attracted considerable attention from academics, companies, and policy makers throughout the world. The main driver is the use of the oil as a replacement for diesel fuel in stationary and instationary internal combustion engines, particularly as the majority of the oils from several varieties is toxic and as such does not compete directly with the food sector. However, the oil also has high potential to be used as input for the oleochemical industry [1], a global business with a volume of about 18 million tonnes (2004) [2].

Pure plant oil derivatives with branches in the fatty acid chains have interesting properties. Branched fatty acids and esters can be applied in a number of products, including surfactants, fabric conditioners, textile auxiliaries, fiber treating agents, hair treating agents, cosmetics, lubricants, additives for fuels and lubricants, rolling and drawing oils, and also as solvents for printing inks [3-11]. Advantages of branched derivatives compared to linear ones are a lower melting point, distinctly reduced pour points, better oxidative stability due to a lower content of carbon-carbon double bonds, and improved lubrication ability. Applications areas are for instance the use as biolubricants or additives in biodiesel to improve the cold flow properties. Available synthetic methodology for the introduction of branches is, among others, epoxidation or dihydroxylation of the carbon-carbon double bonds in the triglyceride structure followed by esterification or etherification with alcohols, short chain carboxylic acids, or acid anhydrides [12-19].

We here report the synthesis of novel branched JO derivatives. The cold flow properties and oxidative stability of the derivatives were determined and compared to virgin JO. Structure-performance relations and particularly the effect of the lengths of the branch and the stereochemistry on cold flow properties were determined. The synthetic methodology involves epoxidised and dihydroxylated JO. As such, the latter two are also interesting reactive building blocks for applications like stabilisers and plasticisers in polymers, as additives in lubricants, as components in plastics and urethane foams, and in general as intermediates for a large number of commodities [3,20,21]. Limited information is available on the catalytic epoxidation and dihydroxylation reactions of JO. The epoxidation of JO with peroxyorganic acids catalysed by acidic ion exchange resins including a kinetic study has been described recently by Goud *et. al.* [20,21].

2.2 Materials and Methods

2.2.1 General

Jatropha oil (JO) originating from Indonesia was obtained from the Bandung Institute of Technology (Bandung, Indonesia) and purified by degumming, neutralisation, bleaching, and deodorisation (*vide infra*). Aqueous hydrogen peroxide (30%-w), ethyl acetate (≥99.0%), acetic anhydride (≥98.0%), sodium chloride (≥99.5%) and activated carbon, were obtained from Merck (Darmstadt, Germany). Methyl tert-butyl ether (98.0%), 4-dimethylaminopyridine (DMAP, 99.0%), hexanoic anhydride (97.0%), NMO(97.0%), ammonium-12-

molybdophosphate hydrate, Al_2O_3 (basic, activated, Brockmann I, ~150 mesh, surface area 155 m^2/g), citric acid (99.5%), Quantofix® peroxide test sticks 1-100 mg/L, chloroform-D1 (99.8 atom %D), Fuller's earth (100-200 mesh) and N,O-bis(trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (99.0%, 1% TMCS) were obtained from Aldrich (Steinheim, Germany). Osmium tetroxide (≥99.9%), Celite® 545, ammonium hydroxide solution (≥25% NH_3 in H_2O), and trimethylsulfonium hydroxide (0.25 M in methanol) were obtained from Fluka (Buchs, Switzerland). Methyltrioxorhenium (98.0%) was obtained from Alfa Aesar (Sulzbach, Germany). Diethyl ether (>99.0%), dichloromethane (99.9%), pyridine (≥99.0%), and methanol (99.9%) were from Lab-Scan (Gliwice, Poland). Magnesium sulfate (dried) was from Boom BV (Meppel, the Netherlands). All chemicals were used as received.

2.2.2 Analytical Methods

The ^1H NMR and ^{13}C NMR were recorded in $CDCl_3$ as the solvent at RT using a Varian AS400 NMR Spectrometer. For ^1H NMR spectra, a total of 64 scans was performed, 4000 scans were recorded for ^{13}C NMR spectra with a relaxation delay of 5 s.

The quantification and compositional analysis of the fatty acids were performed by GC using an HP 5890 model equipped with an HP5 solgel-1MS column (length 30 m, inside diameter 0.25 mm, film 0.25 μm) and an FID detector. GC-MS spectra for structural analysis of the products were recorded on a HP 6890 equipped with an HP1 5973 column (length 30 m, inside diameter 0.25 mm, film 0.25 μm) and a mass selective detector. For both GC's, injection and detection were performed at 275 ^oC and the column temperature was set at 180 ^oC. Before analyses, the products were transmethylated according to a published procedure [22] using trimethylsulfonium hydroxide (0.25 M in methanol). A typical product (100 mg) was dissolved in methyl tert-butyl ether (5 mL). A sample (130 μL) was taken, placed in a 2 mL autosampler vial with insert, and trimethylsulfonium hydroxide (70 μL) was added. The vial was capped and hand-shaken for around 30 s and subsequently 1 μL of the sample was injected into the GC.

Hydroxylated JO samples were silylated before GC analyses to determine the structure and position of the OH groups according to a published procedure [23]. The samples were first transmethylated according to the procedure given above. Subsequently, the solvent was removed by passing a nitrogen flow over the samples. The transmethylated samples (1-5 mg) were placed in a 2 mL autosampler vial with insert and pyridine (100 μL) and the silylating reagent (N,O-bis(trimethylsilyl) trifluoroacetamide) (100 μL) were added. The vial was capped and heated to 60 °C for 20 min and the sample was subsequently analysed by GC.

GPC analyses were performed on an Agilent HPLC 1100 system. Three columns (mixed E, length 300 mm, inside diameter of 7.5 mm) were used. Polystyrene samples with different molecular weights were used for calibration purposes. In a typical analysis, the product (20 mg) was dissolved in THF (2 mL), filtered using a PTFE filter (0.2 μm pores size) and injected.

The cloud and pour point were determined using a Mini Pour/Cloud Point tester model MPC-102A/102L from Tanaka Scientific Limited, Tokyo, Japan, with detection interval of 1 ^{o}C. The L mode was used for virgin JO and the UH mode for modified oils.

DSC analyses were conducted using a DSC 2920 from TA Instrument with a heating rate of 10 ^{o}C/min and a cooling rate of 2 ^{o}C/min. The crystallisation temperature was defined as the temperature at the minimum of the exothermic peak, while the melting point was taken as the temperature at the maximum of the endothermic peak. Since JO and its modified products contain a range of different fatty acid chains, at least two melting and crystallisation temperatures were observed [24]. The melting points and crystallisation temperatures of the products provided in this paper are those of the largest peak.

The oxidative stability of the products was determined using an 873 Biodiesel Rancimat from Metrohm Ion Analysis, Herisau, Switzerland, using air and an operating temperature of 110 ^{o}C.

Elemental analyses (C and H content) were carried out using an automated Euro EA3000 CHNS analyser with acetanilide as a calibration reference. All samples were analysed at least in duplicate and the average value is given.

The oxirane number of epoxidised JO was determined with a non-aqueous titration method according to a procedure reported by Jay [25].

The acid value of the products was determined using a slightly modified procedure reported by the National Cottonseed Products Association (Method number 28.029). The product (0.1 g) was weighed, mixed with diethyl ether and ethanol (50/50 %-v/v) solution (20 mL), and then titrated with a 0.01 N KOH solution in ethanol using phenolphthalein as the indicator until a faint red colour appeared and persisted for at least 30 seconds..

The peroxide content was determined by a titration method. The oil sample (5 g) was dissolved in chloroform-acetic acid solution (30 mL, 50/50 %-v/v). Saturated KI solution (0.5 mL) was added and the biphasic system was mixed by occasional swirling for 1 minute. Water (30 mL) was added and the mixture was titrated directly with a 0.01 N $Na_2S_2O_3$ solution until the yellow colour turned almost colourless. A starch indicator solution (two drops) was added and the titration was continued until the blue color disappeared.

The viscosity of JO was determined using a cone-and-plate viscometer of the type rheometer AR1000-N from TA Instrument with a cone diameter of 40 mm and a 2^{o} angle. The viscosity measurements were conducted at 40 ^{o}C with a shear rate of 15 s^{-1}.

The density of JO was measured at RT using a standard laboratory liquid pycnometer.

2.2.3 Purification of JO

Crude JO was first degummed using a slightly modified procedure as given in ref. 26. Crude JO (6 L) was heated to 70 ^{o}C and an aqueous citric acid solution (600 mL, 3 wt% citric acid) was added to the oil. The mixture was stirred thoroughly at this temperature for 10 min. Thereafter, the solution was cooled to RT and centrifuged at 6000 rpm for 1 h. The degummed oil was mixed with an ammonium hydroxide solution (≥25% NH_3 in H_2O, 600 mL) and stirred thoroughly at RT for 1 h, then kept undisturbed for 6 h to precipitate the soap. The solution was then centrifuged at 6000 rpm for 1 h. Water (2.5 L) was added to the centrifuged oil to remove the remaining soap. This washing step was repeated three times. The oil was then centrifuged again at 6000 rpm for 1 h to separate the remaining water and impurities. Subsequently, the oil was bleached. For this purpose, the neutralised oil was heated to 70 ^{o}C and Fuller's earth (10 wt%) was added to the solution. The suspension was stirred thoroughly at this temperature for 10 min and then cooled to RT and centrifuged at 6000 rpm for 1 h. Deodorisation was performed using a method adapted from ref. 27. The bleached oil was heated up to 100 ^{o}C for 1 h under vacuum (5 mm Hg). The volatile impurities were condensed and removed as distillate. The deodorised oil was cooled down, stored under nitrogen, and analysed by a variety of techniques (Table 1, 2, and 3). Elemental analysis, calculated: C 77.3%, H, 11.7%. Found: C 77.1%, H, 11.8%.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 0.83-0.87 (C***H***$_3$CH$_2$), 1.18-1.58 (-C***H***$_2$-), 1.96-2.05 (-C***H***$_2$CH=CH-), 2.26-2.31 (-C***H***$_2$COO-), 2.73-2.76 (=CHC***H***$_2$CH=), 4.09-4.29 (OCH(C***H***$_2$)$_2$), 5.27 (OC***H***(CH$_2$)$_2$), 5.31-5.36 (-C***H***=C***H***-). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm): 14.3-14.4 (***C***H$_3$CH$_2$), 22.8-34.4 (-***C***H$_2$-), 62.2 (OCH(***C***H$_2$)$_2$), 69.1 (-O***C***H(CH$_2$)$_2$), 128-130 (***C***H=***C***H), 173.0 (-***C***OO-).

2.2.4 Catalytic reactions

2.2.4.1Synthesis of epoxidised JO (1)

JO (105 g, 392 mmol C=C), methyltrioxorhenium (0.5 g, 0.5 mol% ratio to C=C), dichloromethane (79 mL, 5 M of C=C in dichloromethane), and pyridine (4 mL, 12 mol% to C=C) were placed in a three necked round bottom flask and stirred thoroughly at RT. The reaction was initiated by the dropwise addition of aqueous H_2O_2 (30 wt%, 80 mL, 785 mmol). Samples were taken periodically and analysed using ^{1}H and ^{13}C NMR to monitor the conversion. After complete conversion of the carbon-carbon double bonds (1.5 h), dichloromethane (100 mL) was added and the mixture was centrifuged to separate the aqueous and organic layer. The organic phase was passed through an Al_2O_3 column to remove the catalyst. The remaining peroxide was extracted using a brine solution until no peroxide was left in the mixture (peroxide test paper as indicator) and dried over $MgSO_4$. The dichloromethane was removed by vacuum distillation (35 ^{o}C, 100 mbar). The isolated yield of the resulting colourless oil (**1**) was 107 g (96 wt% of theoretical yield). Elemental analysis, calculated: C 73.0%, H 11.0%. Found: C 73.8%, H 11.3%. Oxirane number: 5.1 %.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 0.83-0.89 (C***H***$_3$CH$_2$), 1.22-1.58 (-C***H***$_2$-), 1.68-1.73 (-CHOCHC***H***$_2$CHOCH-), 2.26-2.31 (-C***H***$_2$COO-), 2.86-3.09 (-C***H***OC***H***-,

epoxide), 4.09-4.28 (OCH(C***H***$_2$)$_2$), 5.23 (OC***H***(CH$_2$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm): 11.5-11.6 (***C***H$_3$CH$_2$), 22.3-54.8 (-***C***H$_2$-), 57.2 (-C***H***O***C***H-), 62.2 (OCH(***C***H$_2$)$_2$), 69.1 (-O***C***H(CH$_2$)$_2$), 171 (-***C***OO-).

2.2.4.2 Synthesis of trans-hydroxylated JO (2)

JO (25 g, 93 mmol C=C) was reacted with a mixture of formic acid (28.2 mL, 747 mmol) and aqueous H_2O_2 (30 wt%, 19 mL, 187 mmol) in a three-necked round bottom flask equipped with a magnetic stirrer at RT for 24 h. Subsequently, the organic phase was extracted with diethyl ether (150 mL) and washed several times with brine solution until no peroxide was left in the mixture (peroxide test paper as indicator). The organic layer was centrifuged to remove the remaining water and dried over $MgSO_4$. Diethyl ether was removed by vacuum distillation using a rotary evaporator (T= 30 ^{0}C, p = 200 mbar). Isolated yield: 25.4 g (87 wt% of theoretical yield). Elemental analysis, calculated: C 67.3%, H 11.2%. Found: C 68.2%, H 10.6%.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 0.81-0.84 (C***H***$_3$CH$_2$), 1.20-1.55 (-C***H***$_2$-), 1.99-2.01 (CHOHC***H***$_2$CHOH), 2.24-2.31 (-C***H***$_2$COO-), 3.33-3.97 (C***H***OH, *trans*-dihydroxyl), 4.07-4.25 (OCH(C***H***$_2$)$_2$), 4.82-5.00 (C***H***OCOH), 5.22 (OC***H***(CH$_2$)$_2$), 8.00-8.31 (CHOCO***H***). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C(ppm): 14.9-15.1 (***C***H$_3$CH$_2$), 23.5-39.6 (-***C***H$_2$), 62.3 (OCH(***C***H$_2$)$_2$), 69.0 (-O***C***H(CH$_2$)$_2$), 72.5-75.5 (***C***HOH), 80.2-83.1 (***C***HOCOH), 161-163 (CHO***C***OH), 173-174 (-***C***OO-).

2.2.4.3 Synthesis of cis-hydroxylated JO (3)

JO (15.5 g, 58.0 mmol C=C), osmium tetroxide (167 mg, 0.58 mmol), NMO(10 g, 85 mmol), H_2O (50 mL), and *tert*-butanol (150 mL) were mixed at 60 ^{0}C for 18 h under vigorous stirring. After 18 h, the reaction mixture was filtered through a Celite 545 column. The column was washed with brine (100 mL) and diethyl ether (100 mL). The combined liquids were separated by centrifugation. The organic layer was washed ten times with brine (100 mL each), and dried over $MgSO_4$. Diethyl ether was removed by vacuum distillation using a rotary evaporator (T = 30 ^{0}C, p = 200 mbar and then at T = 75 ^{0}C, p = 100 mbar). Isolated yield: 8.36 g (48 wt% of theoretical yield). Elemental analysis, calculated: C 68.6%, H 11.0%. Found: C 69.0%, H 11.1%.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 0.77-1.00 (C***H***$_3$CH$_2$), 1.20-1.75 (-C***H***$_2$-), 2.25-2.55 (-C***H***$_2$COO-), 3.45-3.85 (C***H***OH, *cis*-dihydroxyl), 4.10-4.38 (OCH(C***H***$_2$)$_2$), 5.25 (OC***H***(CH$_2$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm): 13.8-14.2 (***C***H$_3$CH$_2$), 22.5-34.6 (***C***H$_2$), 62.6 (OCH(***C***H$_2$)$_2$), 69.0 (-O***C***H(CH$_2$)$_2$), 73.5-75.5 (-***C***HOH), 172-174 (-***C***OO-).

2.2.4.4 Synthesis of trans- di-esters from epoxidised JO (4a and 4b)

1 (40 g, 141 mmol of epoxide) was allowed to react under vigorous stirring with acetic anhydride (67 mL, 5 folds molar excess of anhydride to epoxide) or hexanoic anhydride (168 mL), catalysed by AMP (26.5 g, 14.1 mmol) at 75 ^{0}C, with ethyl acetate (400 mL) as the solvent. The colour of the reaction mixture changed from yellow to light green to dark green-blue. ^{1}H NMR analysis revealed that the

reaction was complete after the last colour change. The typical reaction time was 12 h for acetylation and 48 h for hexanoylation. The reaction mixture was then cooled to RT before purification.

For **4a**, a mixture of water and ethyl acetate (200 mL, 50/50 %-v/v) was added slowly under vigorous stirring at 15 °C. The catalyst and the water were separated by centrifugation. Activated carbon black (10 g) was added to the organic layer and stirred for 30 minutes. The mixture was then centrifuged, the organic layer was decanted and washed four times with brine (100 mL each) to extract the excess of acetic acid and subsequently dried using $MgSO_4$. Ethyl acetate was removed by vacuum distillation using a rotary evaporator (T= 70 °C, p=100 mbar). Isolated yield: 5.7 g (10.0 wt% of theoretical yield).

For **4b**, ethyl acetate (100 mL) and activated carbon black (10 g) were added and the suspension was mixed for 30 minutes. Thereafter, the suspension was centrifuged and the liquid phase was separated by decantation. Ethyl acetate was removed by vacuum distillation using a rotary evaporator (T= 70 °C, p= 200 mbar). Methanol was added in a large excess to precipitate the product. This step was repeated several times until no hexanoic anhydride was left in the precipitate (monitored by ^{1}H NMR). The remaining solvents were then removed by vacuum distillation using a rotary evaporator (T = 60 °C, p=30 mbar). Isolated yield: 8.6 g (7.9 wt% of theoretical yield). Elemental analysis, calculated: C 71.1%, H 10.8%. Found: C 71.0%, H, 10.7%.

2.2.4.5 Synthesis of di-esters from trans-hydroxylated JO (5a and 5b)

2, (10 g, 48 mmol of hydroxy groups) was placed in a 100 mL three necked round bottom flask containing DMAP (70 mg, 0.6 mmol) as catalyst. Then acetic anhydride (5.6 mL, 60 mmol) or hexanoic anhydride (14.2 mL, 60 mmol) and pyridine (4.8 mL, 60 mmol) were introduced to the mixture. The reaction mixture was thoroughly stirred at RT for 7 h, or at 50, 80, and 100 °C each for 4 h. Thereafter the reaction mixture was cooled to RT.

For **5a**, a mixture of water and ethyl acetate (50 mL, 50/50 %-v/v) was added slowly under vigorous stirring at 15 °C. The organic layer was separated from the mixture by centrifugation and then washed several times with brine to extract the excess of acetic acid. Ethyl acetate was then removed by vacuum distillation using a rotary evaporator (T= 70 °C, p= 200 mbar). Isolated yield: 5.73 g (43 wt% of theoretical yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm):0.73-0.75 (C***H***$_3$CH$_2$), 1.14-1.48 (-C***H***$_2$), 1.96-2.02 (-CHOCOC***H***$_3$, acetate branch), 2.19-2.22 (-C***H***$_2$COO-), 3.33-3.97 (C***H***OH, *trans*-dihydroxyl), 3.99-4.19 (OCH(C***H***$_2$)$_2$), 4.87-4.98 (-C***H***OCOCH$_3$, acetate branch), 5.14 (OC***H***(CH$_2$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm): 14.2-14.3 (***C***H$_3$CH$_2$), 21.1-35.6 (-***C***H$_2$), 62.2 (OCH(***C***H$_2$)$_2$), 69.0 (O***C***H(CH$_2$)$_2$), 72.5-74.0 (-***C***HOCOCH$_3$, acetate branch), 75.0-76.1 (***C***HOH), 80.2-83.1 (***C***HOCOH), 170-171 (CHO***C***OCH$_3$, acetate branch), 173 (-***C***OO-).

For **5b**, a large excess of methanol was added to precipitate the product. The liquid phase was then removed by decantation. The precipitate was washed several

times with methanol until all hexanoic anhydride was removed (monitored by ^{1}H NMR). The excess of methanol was then removed by vacuum distillation using a rotary evaporator (T = 60 ^{o}C, p= 200 mbar). Isolated yield: 7.84 g (45 wt% of theoretical yield). Elemental analysis, calculated: C 70.7%, H 10.7%. Found: C 69.8%, H 10.6%.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H (ppm): 0.78-0.92 (C***H***$_3CH_2$), 1.19-1.62 (-C***H***$_2$-), 2.25-2.40 (-C***H***$_2$COO-), 3.33-3.97 (C***H***OH, *trans*-dihydroxyl), 4.02-4.32 (OCH(C***H***$_2)_2$), 4.86-5.11 (***C***HOCO$(CH_2)_4CH_3$, hexanoate branch), 5.19-5.25 (OC***H***$(CH_2)_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ_C (ppm): 14.1 (***C***H_3CH_2), 22.5-35.7 (-***C***H_2-), 62.3 (OCH(***C***$H_2)_2$), 69.1 (-O***C***H$(CH_2)_2$), 74.5-75.5 (-***C***HOCO$(CH_2)_4$CH, hexanoate branch), 76.0-77.1 (***C***HOH), 80.2-82.8 (***C***HOCOH), 173-174 (-***C***OO-).

2.2.4.6 Synthesis of a di-esters from cis-hydroxylated JO (6)

6 was prepared from **3** using the same reaction conditions as for the preparation of **5b**. **3** (7.25 g, 43.2 mmol of hydroxy groups) was reacted with hexanoic anhydride (10.3 mL, 43.2 mmol) catalyzed by DMAP (52.8 mg, 0.43 mmol) and pyridine (3.5 mL, 43.2 mmol). The reaction was performed at 80 ^{o}C for 4 h. The purification method was the same as for **5b**. Isolated yield: 6.8 g (43 wt% of theoretical yield). Elemental analysis, calculated: C 70.5%, H 10.7%. Found: C 71.3%, H 11.0%.

2.3 Results and Discussion

The branched Jatropha oil derivatives described in this paper contain vicinal ester groups in the fatty acid chains of the triglyceride. The length of the ester branches (methyl and n-pentyl) as well as the stereochemistry of the vicinal ester groups (*cis* or *trans*) were varied. The branched compounds were synthesised according to a number of catalytic steps involving epoxides and vicinal diols as the intermediate products (Fig. 1). In the following, the synthetic procedures, including optimisation studies to improve yields and reduce by-products, will be reported. The products were characterised with a variety of techniques (e.g. ^{1}H and ^{13}C NMR, GC-MS, and GPC analysis) and relevant features will be reported. Finally, relevant product properties and particularly cold flow properties and oxidative stability will be discussed.

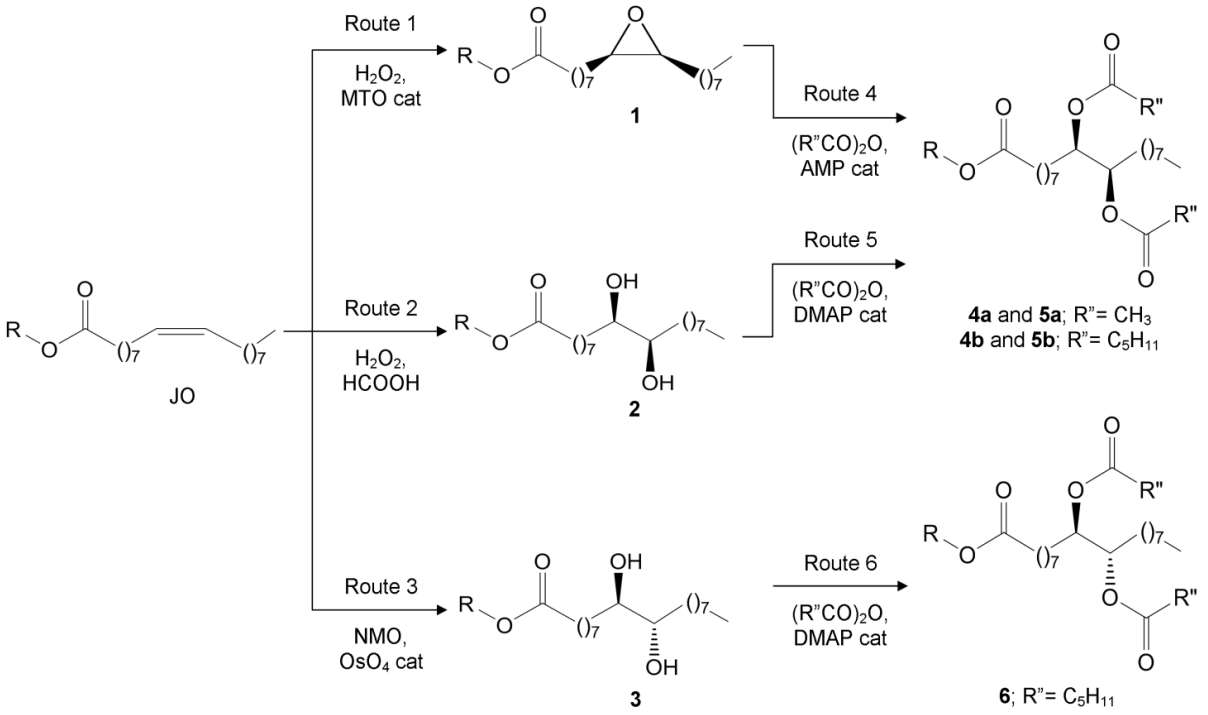

Fig. 1 Overview of JO modification chemistry. R = remaining triglyceride structure. (JO is a triglyceride consisting of different saturated and unsaturated fatty acids, see Table 1, and for brevity, only a mono-unsaturated fatty acids is given. Also only one representative compound of the racemic mixture is shown for each step)

2.3.1 Characterisation of the Jatropha oil feedstock

The Jatropha oil used in this investigation was obtained from Indonesia and purified before use by a four step procedure. Relevant oil properties are given in Table 1-3. The composition of the fatty acid chains was determined by GC (Table 1) and the oil was shown to have a high level of unsaturation (79.2 mol%). The fatty acid profile is in general within the broad range for JO reported in the literature [28]. With this data available, relevant data like the number of carbon-carbon double bonds and the average molecular weight of the triglyceride can be calculated (Table 2). This information was used to determine catalysts and reagents intakes for the subsequent catalytic modification reactions. These characteristics were also determined from ^{1}H NMR measurements (Table 2) and compared with the GC-FID data. Good agreement between both methods was observed. A typical ^{1}H NMR spectra of JO is depicted in Fig. 2(a), showing the presence of the H atoms attached to the carbon-carbon double bonds (peaks in the region of δ 5.3 - 5.4 ppm) and in the range of δ 2.6 - 2.8 ppm for the allylic -CH_2- moiety between two adjacent carbon-carbon double bonds.

Table 1 Fatty acid composition of JO

Fatty acid		Composition [%-mol], GC-FID	Composition [%], literature data [28]
Myristic acid	14:0	-	0 - 0.1
Palmitic acid	16:0	13.7	14.1 - 15.3
Palmitoleic acid	16:1	-	0 - 1.3
Stearic acid	18:0	7.1	3.7 - 9.8
Oleic acid	18:1	50.3	34.4 - 45.8
Linoleic acid	18:2	28.9	29.0 - 44.2
Linolenic acid	18:3	-	0 - 0.3
Arachidic acid	20:0	-	0 - 0.3
Behenic acid	22:0	-	0 - 0.2
Total unsaturated acids fraction		**79.2**	**63.4 - 91.6**

Table 2 Quantitative comparison between ^{1}H-NMR and GC-FID result for JO

Parameter	^{1}H-NMR	GC-FID
Average number of double bonds in a fatty acid chain	1.13	1.08
fraction of di-unsaturation in unsaturated C18 fraction	0.39	0.37[‡]
fraction of unsaturated fatty acids	0.78	0.79
average carbon length of fatty acid chain	17.3	17.7

[‡]mole fraction of linoleic acid compared to the mole fraction of all C18 unsaturated fatty acids in JO.

Relevant physical and chemical properties of the crude and purified JO are given in Table 3. The peroxide value of the purified oil was 1.82 meq/kg and the acid value was 0.19 mg KOH/g. These values are considerably lower than found for the crude JO (acid value of 4.6 mg KOH/g and a peroxide value of 5.3 meq/kg), a clear indication that the purification procedure was successful. Typical literature values for JO are an acid value of 4.5 mg KOH/g and a peroxide value of 1.93 meq/kg [29].

Table 3 Physical and chemical properties of JO used in this study

Properties	Crude JO	Purified JO	unit
Acid value	4.6	0.19	mg KOH/g
Peroxide value	5.3	1.82	meq/kg
Density at rt	n.d.[a)]	0.88	g/mL
Viscosity at 40 °C	n.d.[a)]	42	cSt

[a)]not determined

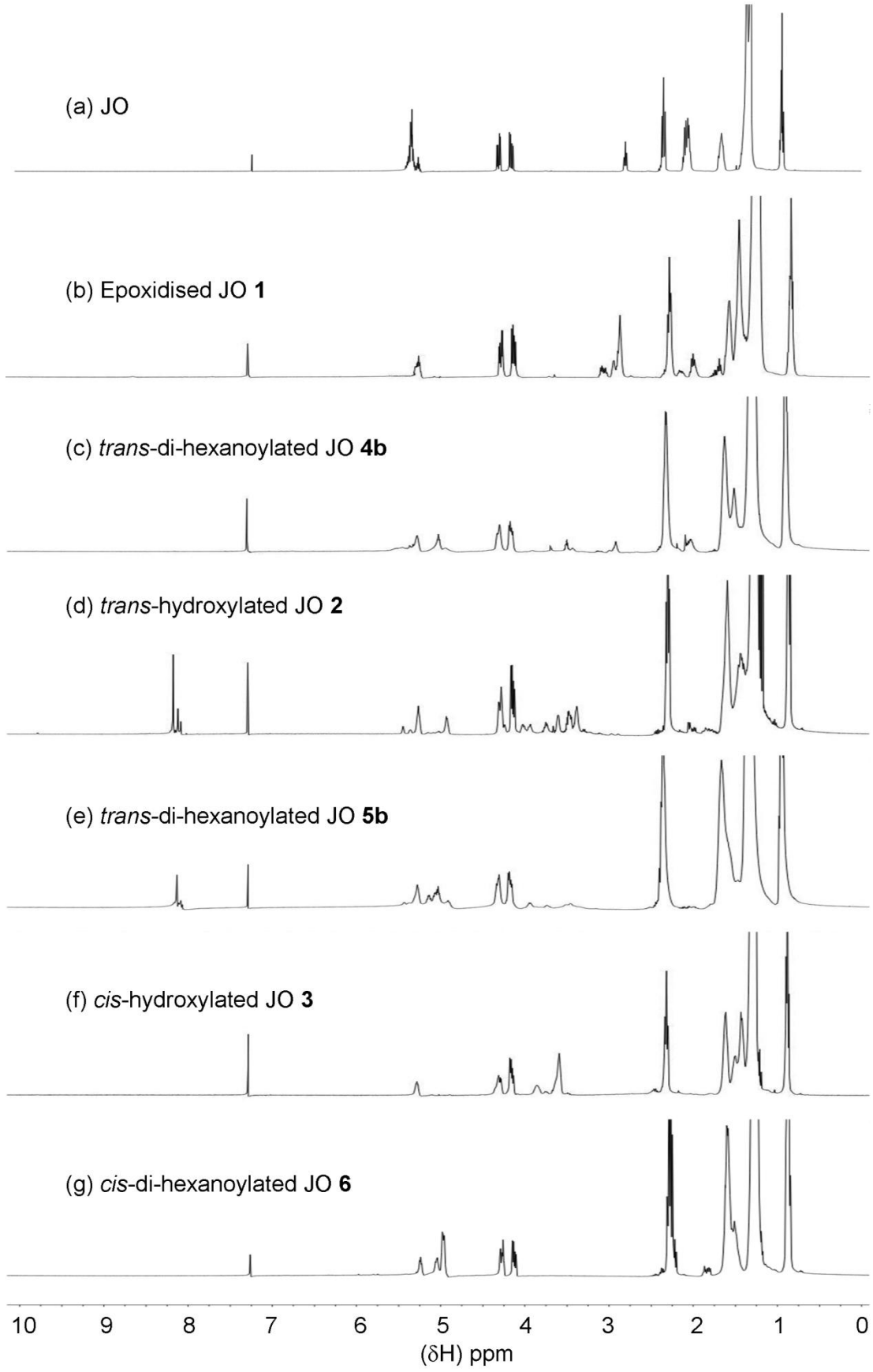

Fig. 2 Typical ^{1}H NMR spectra ($CDCl_3$) of JO and derivatives

2.3.2 Synthesis of epoxidised JO (1)

1 was prepared using a well-known selective epoxidation route developed by Sharpless and co-workers [30] using MTO as the catalyst and hydrogen peroxide as the oxidant. **1** was obtained as a transparent colourless liquid in essentially quantitative yields (96 wt%) and characterised by ^{1}H and ^{13}C NMR as well as GC-MS analysis. The oxirane number as determined by titration was 5.1 %, which is below the commercial specification for epoxidised oils (6.5 %) [31] and is as expected lower than the maximum value for an epoxidised JO (5.4 %) predicted by Meyer *et. al.* [32]. A typical ^{1}H NMR spectrum is given in Fig. 2(b). Complete conversion of the carbon-carbon double bonds is observed and the characteristic peaks of olefinic and allylic hydrogen atoms at δ 5.3 - 5.4 ppm and δ 2.6 - 2.8 ppm are absent. New peaks from the hydrogen atoms on the epoxide units are present in the region of δ 2.8 - 3.1 ppm. Hydrolysis and the formation of diols do not occur under these conditions, as is evident from the absence of new peaks in the range of δ 3.3-4.0 ppm.

GC-MS analysis shows the presence of both mono- and di-epoxides in the products, from the epoxidation of the oleate and linoleate fatty acid chains, respectively [33]. The stereochemistry of the epoxide units was not established. However, the Sharpless epoxidation route is known to provide epoxides in the *cis-cis* configuration [34] and this is expected to be the case for JO as well.

2.3.3 Synthesis of *trans*-hydroxylated JO (2) and *cis*-hydroxylated JO (3)

For the synthesis of hydroxylated JO, two well-known methods were explored, i.e. a Prilezhaev dihydroxylation using performic acid [35] and an Upjohn dihydroxylation using osmium tetroxide as catalyst and NMO as the oxidant [36,37]. These methods result in different product stereochemistry, i.e. the *trans*-vicinal diols (**2**) from the Prilezhaev hydroxylation and the *cis*-vicinal diols (**3**) from the Upjohn hydroxylation.

The Prilezhaev method using *in situ* generated performic acid from hydrogen peroxide and formic acid gave **2**, as colorless oil in 87 wt% yield. ^{1}H NMR showed that the carbon-carbon double bond conversion was essentially quantitative (96 mol%, see Fig. 2(d) for details). Resonances of the -C*H*-OH units appear in the region of δ 3.33-3.97 ppm. Interestingly, also some peaks are present in the region δ 8.0-8.3 ppm. These are typical for formyl branches [38], known to be formed when the intermediate epoxide is reacting with formic acid instead of water. Based on peak areas, the selectivity to diols is about 80% and about 20% for formyl branches.

cis-Dihydroxylation of JO was performed using osmium tetroxide as the catalyst and NMO as the oxidant at 60 °C for an 18 h reaction time. The solid product (**3**) was isolated in 48 wt% yield. According to ^{1}H NMR, full conversion of the carbon-carbon double bonds to diols was achieved (Fig. 2(f)). Characteristic resonances from the *cis*-diols appear in the region δ 3.45-3.85 ppm.

Both the *trans*- and *cis*-diols were also characterised using GC-MS after methylation (of the glycerol unit) and silylation of the -OH groups on the fatty acid chains with N,O-bis(trimethylsilyl)trifluoroacetamide. Clear GC peaks with characteristic mass fragmentation patterns were observed for 9,10-dihydroxystearate

and 9,10;12,13-tetrahydroxystearate units, the result of a single dihydroxylation of oleic and a double dihydroxylation of linoleic units in the JO, respectively [39].

2.3.4 Synthesis of branched vicinal di-esters from epoxidised and hydroxylated JO (4a, 4b, 5a, 5b, 6)

The introduction of the ester groups on the fatty acid chains of the triglyceride was performed by reaction of either the epoxide groups of **1** or hydroxyl groups of the dihydroxylated compounds with anhydrides. To gain insights in the length of the ester branch on relevant product properties, acetic- and hexanoic anhydride were used.

2.3.4.1 Epoxide ring opening with anhydrides (Fig. 1, route 4)

For the ring opening of **1** with anhydrides, a published procedure was used involving AMP as the catalyst [40]. This catalyst has so far only been used for small epoxides such as styrene oxide, cyclopentane oxide, and cyclohexane oxide, and also not for the esterifications using anhydrides with chain lengths longer than acetic anhydride. The use for triglycerides is a novelty of this paper. The synthetic methodology is known to result in vicinal di-esters in a *trans* configuration. Initially, experiments with JO and acetic anhydride were performed at RT, as described in the literature for small epoxides [40]. However, after 1.5 h reaction time, no conversion was observed.

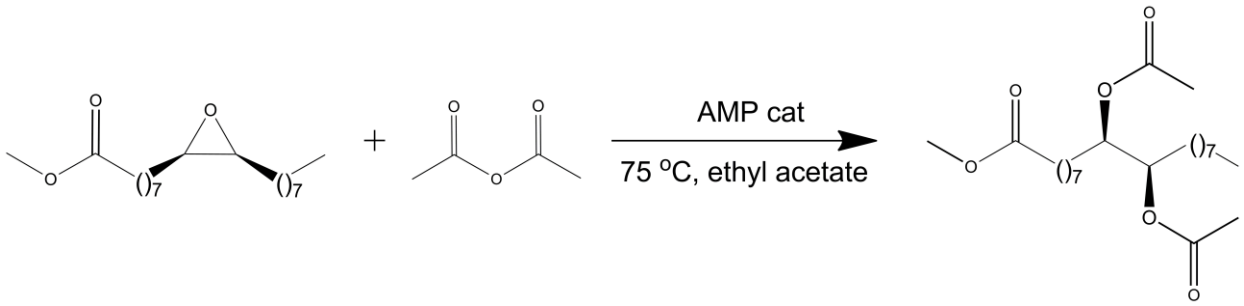

Fig. 3 Model reaction for epoxide ring opening with acetic anhydride

To gain insights in the reaction rates, model studies were performed using epoxidised methyl oleate and acetic anhydride (Fig. 3). At RT, reactions for 23 days only resulted in 75% conversion of the epoxide. Higher reaction rates were observed at elevated temperatures and at 50, 100, 125, and 140 °C, the reactions were finished within 48 h, 1.5 h, 45 min, and 10 min, respectively. The products were analysed using NMR and GPC. Particularly, GPC analysis is very informative and reveals the formation of higher molecular weight (HMW) products besides the epoxide ring opening reaction to produce the di-esters (Fig. 4). Such HMW products are likely formed by cross-linking reactions or self polymerisation reactions of the epoxide groups [16]. Even at the lowest temperature in the range (20 °C), the HMW products were already formed. Such HMW products are expected to have a negative effect on

product properties and some experiments were performed to reduce their formation. The stepwise addition of the epoxide to the reaction mixture gave the best results and the amount of products with molecular weights higher than 1000 Da was considerably, though not quantitatively, reduced (Fig. 4).

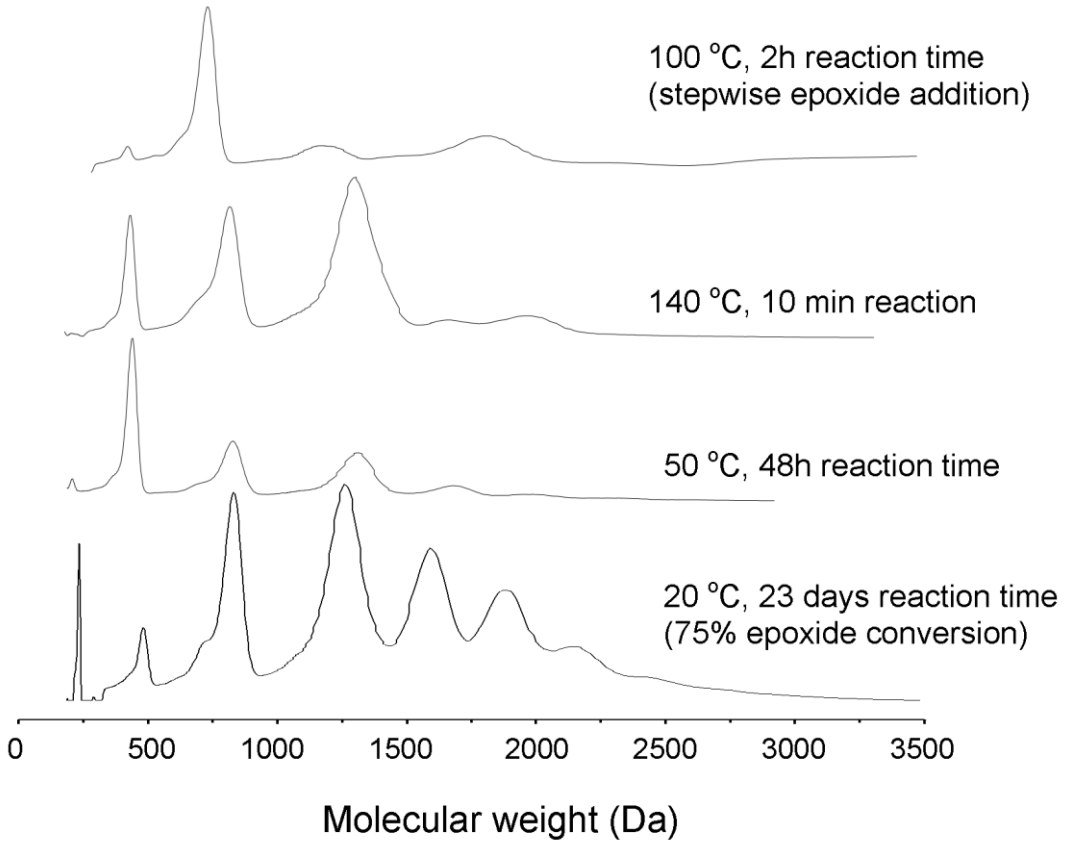

Fig. 4 GPC measurements for reaction products of epoxidised methyl oleate with acetic anhydride using AMP as the catalyst at different reaction times and temperatures (solvent free).

Further improvements were obtained using ethyl acetate as the solvent and an excess of anhydride. At 5-10 wt% intake of epoxidised methyl oleate and the use of a large excess of anhydride on epoxide, the amount of HMW products was reduced further, though not suppressed completely (Fig. 5). We therefore conclude that epoxide ring opening with AMP always leads to the formation of HMW components, the exact amount being a function of temperature, reaction time, dilution level and molar ratios of reactants.

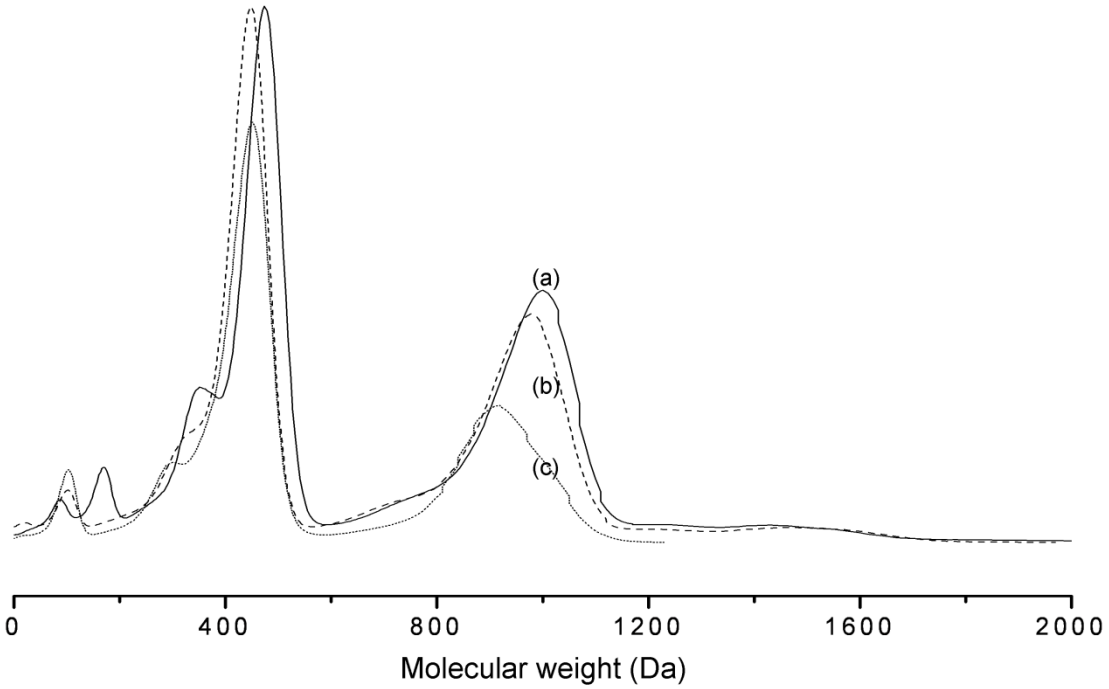

Fig. 5 GPC measurements for reaction products of epoxidised methyl-oleate with acetic anhydride using AMP as catalyst at different solvent intakes and mol ratio's of reactants at 75 °C. Specific reaction conditions: (a) 1 g of epoxide in 10 mL ethyl acetate, reaction time 18 h, epoxide to anhydride ratio 1:5; (b) 1 g of epoxide in 20 mL ethyl acetate, reaction time 20 h; epoxide to anhydride ratio 1:5; (c) 1 g of epoxide in 10 mL ethyl acetate, epoxide to anhydride ratio 1: 65, reaction time 6 h.

1 was esterified with hexanoic anhydride using the optimised conditions for the model reaction between epoxidised methyl oleate and acetic anhydride. The product (**4b**) was obtained as a yellow liquid product. Fig. 2(c) shows a typical ^{1}H NMR spectrum of the product. Characteristic resonances of the di-ester branches are present in the region of δ 4.9 - 5.2 ppm (-C***H***-O-(C=O)-). The presence of some remaining cross-linked products is evident from resonances in the region of δ 3.3-3.7 ppm and δ 4.6-4.9 ppm. This identification is based on peak intensities of samples with various levels of cross linking (as determined by GPC).

In general, the isolated yields of the reaction of **1** with anhydrides were low (< 10%). This is due to a tedious work-up procedure involving multiple extraction and adsorption step to remove the excess of anhydride used in the reaction. Further optimisation studies will be required to optimise the isolated yields.

2.3.4.2 Esterification of dihydroxylated JO derivatives with anhydrides (Fig. 1, route 5 and 6)

The *trans*-hydroxylated JO derivative was esterified with acetic and hexanoic anhydride, while the *cis*-hydroxylated JO was esterified with hexanoic anhydride to obtain the corresponding *cis*- and *trans*- vicinal di-esters. The esterification reactions of **2** (Fig. 1, route 5) were performed with DMAP as the catalyst, a molar ratio of **2** to anhydride of 1 to 1 and in the absence of a solvent. The products were obtained as yellow-to-orange liquids in isolated yields of 43-45%. The effect of temperature (20, 50, 80, and 100 °C) on the hydroxy group conversion at a fixed reaction time of 4 h was determined by ^{1}H NMR and the results are given in Fig. 6. The highest conversions (> 80 %) were observed at 80 °C. Increasing the temperature to 100 °C gave a lower hydroxyl group conversion. Extending the reaction time at 100 °C also did not lead to higher conversions. Thus, it is possible that the reaction is an equilibrium reaction and that full conversion of the hydroxy groups is not possible because of thermodynamic considerations [41]. An alternative explanation is catalyst deactivation at elevated temperatures.

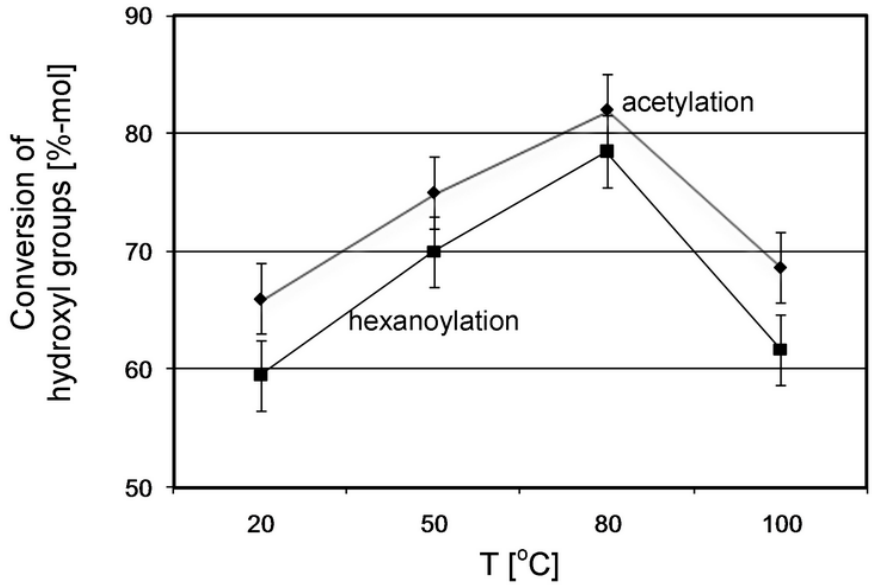

Fig. 6 Hydroxyl group conversion for the reaction of **2** with acetic- and hexanoic anhydride as a function of the temperature (reaction time 4 h, anhydride to **2** molar ratio of 1:1)

Fig. 2(e) shows a typical ^{1}H NMR spectrum for **5b** and particularly the product of the reaction between the **2** with hexanoic anhydride at 80 °C. Clearly visible are the remaining hydroxyl groups in the region of δ 3.3 - 4.0 ppm, whereas protons (-C***H***-O-(C=O)-) of the hexanoic ester branch are in the region of δ 4.8 - 5.2 ppm. In addition, the formyl branches are also still present in the product (8.0-8.3 ppm), an indication that exchange of formyl branches with hexanoic acid branches does not occur under the prevailing conditions. Based on the ^{1}H NMR data it may be concluded that the product **5b** contains both hexanoyl and formyl branches as well as some unconverted -OH groups.

The esterification reaction of **3** with hexanoic anhydride (Fig. 1, route 6) was performed using the same synthetic methodology system as for **2** (DMAP catalyst, 80 °C, 4 h reaction time). The product was obtained as a liquid in 43% isolated yield. Full conversion of the hydroxyl groups was accomplished (^{1}H NMR, see Fig. 2(g)), in contrast with **2**, which has a maximum hydroxyl group conversion of about 80%. This implies that the reaction is likely not an equilibrium reaction and that the experimentally observed incomplete conversions for the *trans*-analogue (*vide supra*, Fig. 6) are kinetic in origin. It also suggests that the reaction of anhydrides with vicinal diols in the *cis*-configuration is much faster than for the *trans* configuration. This conclusion is in line with literature data for the esterification of *cis*- and *trans* vicinal diols [42-44]. For instance, the esterification reaction of a mixture of *cis*- and *trans*-1-ethyl-1,2-cyclobutanediols with methylboronic acid (at RT) gave solely esters of the *cis*-diols, while the *trans*-diols remained unreacted [42].

2.3.5 Product properties

2.3.5.1 Cold flow properties

The cold flow properties of the modified JO products were determined using cloud- and pour point analyses and by DSC (melting and crystallisation temperature). The results of the measurements are given in Fig. 7. The JO feed shows a cloud point of -2 °C and a pour point of -4 °C. These values are in line with literature data, which reported a pour point of -3 °C for JO [45]. The cold flow properties of the JO derivatives are found within a broad range. For instance, the pour points range from -14°C (for **5b**) to -3 °C (for **5a**) whereas the spread in melting points (DSC) is even larger (-10 °C for **1**, vs. 43 °C for **3**). The lowest pour point in combination with lowest crystallisation temperature was found for **5b** (pour point of -14 °C, crystallisation temperature of -25 °C). Thus, considerable improvements in cold-flow properties for JO are possible by the introduction of branches in the fatty acid chains.

Comparison between the cold flow properties of **5b**, with hexanoyl branch, and the related **5a**, with acetyl branch, makes it possible to draw conclusions with respect to the length of the branch. The cloud point, pour point and melting point for **5b**, are lower than for **5a**. A similar trend was observed when comparing the data for **4a** and **4b**. This implies that longer branches lead to improved cold flow properties, which is in line with literature data [14,16,46,47]. For instance, Moser determined the low temperature properties of a range of di-esters derived from oleic acid [46]. The compounds contain and α-hydroxy-ester group in the chain and a terminal ester group. Increasing chain length of the α-hydroxy-ester group was shown to result in improved low temperature properties. It was hypothesised that long chain ester more effectively disrupt crystallisation.

The cold flow properties of the *trans* products obtained by the epoxidation route, **4a** and **4b**, and those of the hydroxylation route, **5a** and **5b**, differ somewhat (Fig. 7). For instance, the crystallisation temperature of **4b** is -18 °C while it is -25 °C for **5b**. The chemical structure of the product is in principle similar, however, the products from the epoxidation route contain some cross-linked products (*vide supra*) and these may be responsible for the differences.

Of interest are also the cold-flow properties of **1,** and particularly the low crystallisation temperature of -27 ^{o}C is worth mentioning. This value is close to that of two literature values for epoxidised soybean oil, being -20 and -25 ^{o}C [48,49]. Apparently, crystallisation is seriously inhibited when epoxide groups are present.

Clear differences in product properties are observed as a function of the stereochemistry of the vicinal diols/ester units. For instance, the cold flow properties of the **5b**, are considerably better than the *cis* analogue, **6**, in all respects (Fig. 7). Apparently, the *trans* structure is favoured for improved cold flow properties. This is also supported by comparing the data for **2** and **3**, the dihydroxylated JO derivatives with vicinal diols structure element. The *cis*-diols, **3,** is solid at RT, with a melting point of 43 °C and a crystallisation temperature of 25 °C (DSC). The *trans* analogue, **2**, is a liquid at RT with a melting and crystallisation temperature of 6 and -1 ^{o}C, respectively. Apparently, in the *cis* orientation, crystallisation is more facile, presumably by improved inter- and/or intra-molecular hydrogen bonding. These differences in properties are in line with available literature data. For instance, a study on *cis*- and *trans*- 1,2-cyclohexanediols properties revealed that the *cis*-diols tends to solidify and has a higher melting point than the *trans*- counterpart [50].

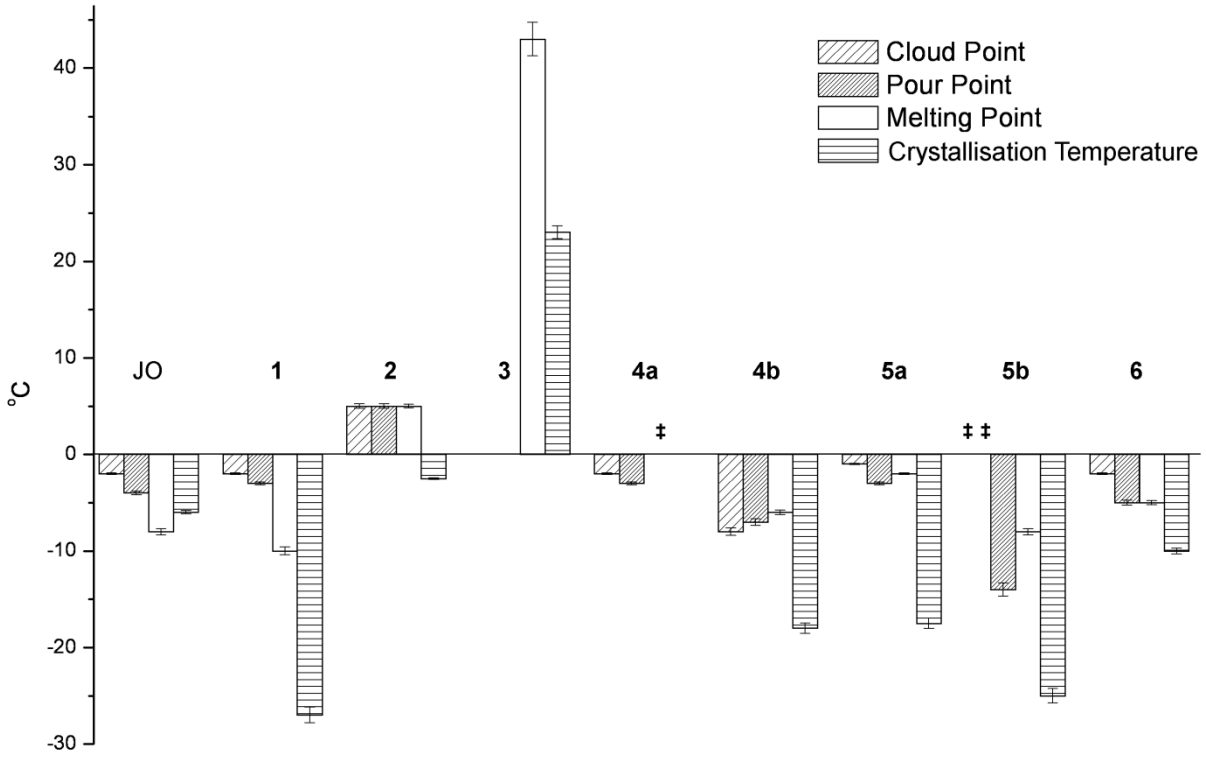

Fig. 7 Summary of cold flow properties of JO and a number of derivatives. ‡ Melting point and crystallisation temperature for **4a** were not determined. ‡‡ No CP was detected.

2.3.5.2 Oxidative stability

The oxidative stability of the products was determined by a standard protocol using a Rancimat device with ambient air as the carrier gas at an operating temperature of 110 ^{o}C. Figure 8 shows the oxidative stability of the hexanoylated

products, **4b**, **5b**, and **6,** and JO as the reference. The purified JO has an oxidative stability time of 12 h (Figure 8, indicated as induction time) after which the conductivity increases rapidly.

For all modified products, the oxidative stability is much better than for JO. The initial conductivity of the modified products is somewhat higher than the original JO, which could be due to the presence of traces of volatile organics (e.g. acid residues). Though speculative, the slow increase in the conductivity in time may be caused by the formation of traces of free acids by hydrolysis of the ester branches.

The improved oxidative properties are in line with expectations as the modified products contain virtually no residual carbon-carbon double bonds, which are the prime cause for the oxidative decay of plant oils and derivatives.

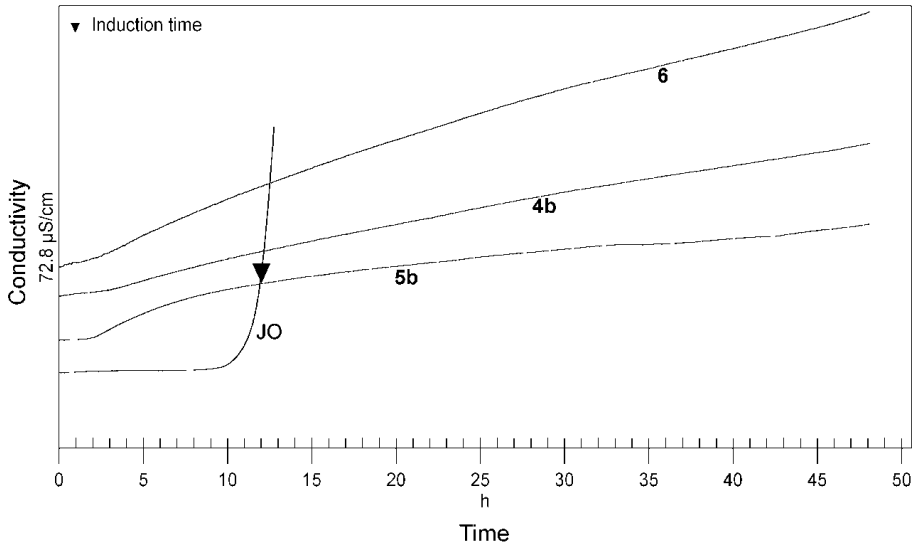

Fig. 8 Oxidative stability of JO and the various hexanoylated derivatives

2.4 Conclusions

The synthesis of a number of branched JO derivatives containing vicinal di-ester units in the fatty acid chains is reported. The cold flow properties (pour- and cloud point, melting point and crystallisation temperature) were determined and shown to be a function of the length of the branches (acetyl versus hexanoyl) and the stereochemistry of the vicinal di-ester units (*cis* versus *trans*). The best cold flow properties (lowest pour and cloud points, crystallisation and melting temperature) were obtained for the longest branch in a *trans* orientation (*trans*-di-hexanoylated JO, **5b**), and were also considerably better than the JO source. The cold flow properties of the corresponding *cis* components (*cis*-hydroxylated JO **3** versus trans-hydroxylated JO **2** and *cis*-di-hexanoylated JO **6** versus its *trans* counterpart **5b**), were considerable less, an indication that the stereochemistry is of prime importance and should be taken into account when developing cold-flow improvers or biolubricants. The oxidative properties of the branched products are considerably

better than for the JO feed, as a result of the reduced number of carbon-carbon double bonds in the structure.

In general, the final products have improved cold flow properties and better oxidative stability compared to that of virgin JO and as such could have interesting industrial applications, for example as biolubricant and cold-flow improvers.

2.5 List of abbreviations

JO : Jatropha curcas L. oil
AMP : ammonium-12-molybdophosphate
DMAP: 4-dimethylaminopyridine
GPC : gel permeation chromatography
DSC : differential scanning calorimetry
HMW : higher molecular weight
MTO : methyltrioxorhenium
NMO : 4-methylmorpholine-N-oxide

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Chapter 3

Application of metal triflate catalysts for the synthesis of higher alcohol esters of *Jatropha curcas* L. oil

Summary

This paper describes an experimental study on the application of metal triflate salts for the (*trans*-) esterification of fatty esters (triolein, methyl oleate, methyl linoleate), fatty acid (oleic acid), as well as *Jatropha curcas* L. oil with methanol and higher alcohols (ethanol, n-propanol, *iso*-propanol, *iso*-butanol, *tert*-butanol). The effect of the metal type (scandium, bismuth, aluminium, lanthanum, copper, zinc) and process conditions to reaction performance were evaluated. Highest conversions were obtained with $Al(OTf)_3$. Reaction of triolein with methanol gave 99 mol% conversion at 165 ^oC for 1h and the main product was the methyl ester. In addition, partial methoxylation of the carbon-carbon double bonds in the fatty acid chains was observed, though the yield was less than 20 mol%. The *trans*-esterification reaction was also successfully performed using higher alcohols, giving > 95 mol% conversions for ethanol, n-propanol, *iso*-propanol and *iso*-butanol, whereas *tert*-butanol was not reactive. For the reaction of oleic acid with methanol, quantitative esterification, partial methoxylation of the carbon-carbon double bonds and the formation of small amounts of a lactone was observed. The methodology using $Al(OTf)_3$ was successfully performed on the *trans*-esterification reaction of JO (FFA content of 2.1 wt%) with various alcohols. Key properties (viscosity, pour- and cloud points) of the (branched) Jatropha esters were determined. The best cold flow properties were obtained for the *iso*-propyl esters of JO, with cloud point (CP) and pour point (PP) of -3 and -24 ^oC, respectively.

Keywords: (*trans*-)esterification, alkoxylation, isomerisation-γ-lactonisation, biodiesel, metal triflates, cold-flow properties

3.1 Introduction

Biodiesel (fatty acid methyl esters) is an important biofuel with an estimated global production volume of nearly 1.1 billion gallons in 2011 [1]. Favourable product properties like high flash point, relatively low viscosity, and only a marginal lower energy content than conventional diesel makes biodiesel a good substitute for fossil diesel in the industry and transportation sector [2].

A point of concern is the cold flow properties, expressed in terms of pour- and cloud point, particularly in countries with winter temperatures below 0 °C, leading to plugging and poor combustion performance [2-4]. The pour point of biodiesel is known to be a function of the degree of unsaturation of the fatty acid chains and the average fatty acid chain length and as such is a function of the plant oil source, see Fig. 1 for details. A combination of a high degree of unsaturation and a higher average chain length leads to a lowering of the pour point and thus has a positive effect on the cold flow properties. This relation only holds for oils with average FA chain lengths between 17 and 19, for oils with a much smaller average chain length, for example coconut oil, this relation does not hold.

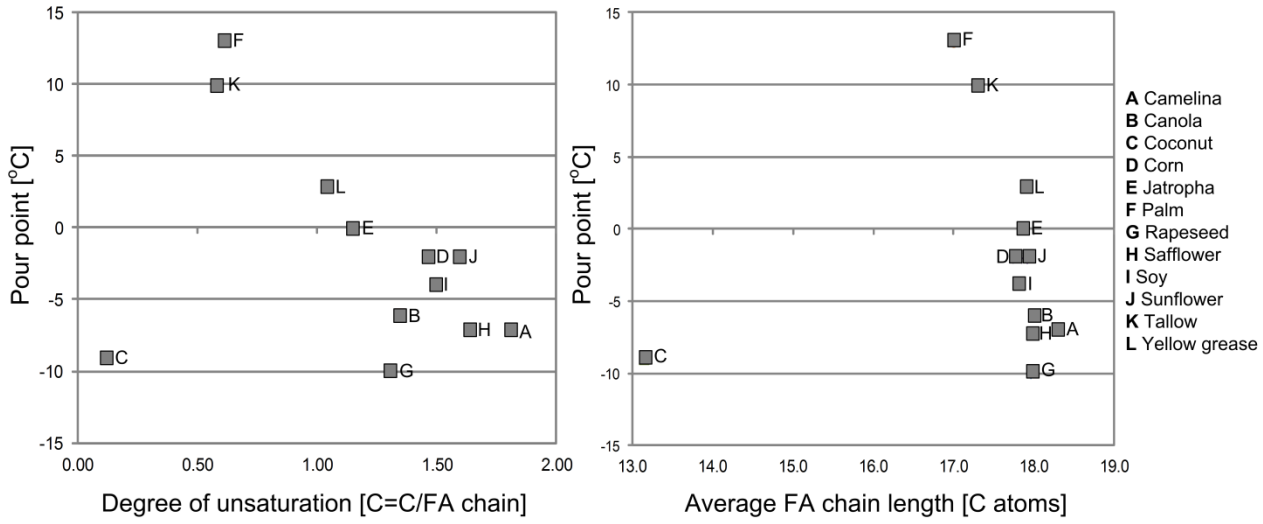


Fig. 1 Effect of a) degree of unsaturation and b) the average chain length of fatty acid methyl esters to pour point property (adapted from ref. 5)

In addition to a proper choice of the pure plant oil source, the use of cold-flow improvers or other alcohols than methanol in the *trans*-esterification reaction have been proposed [6]. An overview on the effect of the application of higher alcohols instead of methanol on cold-flow properties for various plant oil sources is given in Table 1. The use of higher alcohols and particularly branched alcohols instead of methanol in general leads to an improvement in the cold flow properties.

Table 1 Cold-flow properties (CP and PP) of fatty acid alkyl esters[a]

Oil source	Ester group							Ref
	methyl	ethyl	n-propyl	*iso*-propyl	n-butyl	iso-butyl	2-butyl	
Soybean	1.4/1.0		-1.4/-5.0	-8.2/-10.7	-2.9/-5.3	-7.6/-12.0	-7.9/-12.0	7
Canola	1.0/9.0	1.0/6.0		7.0/12.0	6.0/16.0			8
Palm	13.0/16.0	8.0/6.0						8
Safflower	n.a./6.0	6.0/6.0						8
Sunflower	2.0/3.0	1.0/5.0						8
Beef tallow	17.0/15.0	15.0/12.0	12.0/9.0	8.0/0.0	9.0/6.0	8.0/3.0		8

[a)]First value is the CP [^{o}C], second value is the pour point [^{o}C]

Conventional biodiesel synthesis using acid or base catalysis with higher alcohols is often more cumbersome than for methanol [9,10]. Full conversion of the oil is more difficult to achieve due to lower reaction rates [9]. Recently, metal triflate catalysts have been introduced for biodiesel synthesis. Scandium and bismuth triflate were shown to catalyse the (*trans*-) esterification of free fatty acids (FFA) and triglycerides very efficiently [11]. For example, the *trans*-esterification of triolein using scandium or bismuth triflate (10 mol%) and MeOH (48 molar excess) at 150 ^{o}C for 20-25 minutes gave methyloleate in 92% ($Sc(OTf)_3$) and 85% (($Bi(OTF)_3$) yield. For oleic acid, the esterification reaction is much faster at similar conditions and with 1 mol% of catalyst essentially quantitative yields were obtained for $Sc(OTf)_3$ in 1 minute.

We here describe a study on the use of metal triflate catalysts for biodiesel synthesis using higher alcohols. To the best of our knowledge, this is an absolute novelty of this paper and such catalysts have been explored for methanol only. A catalyst screening study on two model reactions viz. the *trans*-esterification of triolein and the esterification of oleic acid using a range of metal triflates is reported. The effects of the length and type of the alcohol (primary, secondary, tertiary) on catalyst performance were studied. Finally, the best catalysts were also tested for a typical example of a plant oil (*Jatropha curcas* L. oil (JO)). Relevant product properties (viscosity, pour and cloud point) of the product esters were determined and structure-property relations were derived.

3.2 Experimental

3.2.1 Materials

Unrefined JO was obtained from Diligent Energy BV (Eindhoven, The Netherlands). The oil was store at 6 ^{o}C for at least 10 h and the residue was filtered [12]. Refined JO was prepared by degumming, deacidification, bleaching, and deodorisation using a method described in [13]. Metal triflate catalysts (> 99.0%), alcohols (> 98.0%, dried using $MgSO_4$ and stored on molecular sieves before use), sodium methoxide (25% in methanol), triolein (> 97.0%), tristearine (> 99.0%), oleic

acid (> 99.0%), methyl oleate (99.0%), triacetine, > 99.0%), methyl tert-butyl ether (98.0%), and chloroform-d (99.8 atom %D) were obtained from Sigma-Aldrich (Steinheim, Germany). $MgSO_4$ (dried) was from Boom BV (Meppel, The Netherlands). All materials were used as received unless otherwise stated.

3.2.2 Methods

Batch experiments in a microwave reactor were performed using a Discover & Explorer SP Microwave Synthesizers from CEM's Focused™ Microwave Technology purchased from Beun de Ronde (Abcoude, The Netherlands). Screening reactions were performed in glass ampoules (outside diameter 8 mm, inside diameter 5 mm, length 15 cm). The ampoules were filled with the reagents and solvent and sealed with a torch. Maximum pressure in both reactor configurations is about 21 bars and this limits the upper temperature of a reaction. Using vapour pressure curves based on the Antoine equation [14], 165 ^oC was selected as the maximum reaction temperature for methanol and 185 ^oC for all higher alcohols.

^1H NMR analyses of JO and derivatives were performed on an Oxford AS400 NMR Spectrometer whereas ^{13}C NMR analyses were performed on an Oxford AS200 NMR Spectrometer. $CDCl_3$ was used as the solvent.

GC-MS spectra for structural analysis of the products were recorded on an HP 5890 equipped with a sol-gel capillary column (length 30 m, inside diameter 0.25 mm, and film thickness 0.25 μm) and a mass selective detector. Peak identification was done using the NIST05a mass spectra library. Helium was used as the carrier gas at a flow rate of 0.6 ml/min. The oven temperature was kept at 120 ^oC for 5 min and heated up to 250 ^oC at a rate of 3 ^oC/min, and then held at 250 ^oC for 15 min. The injector temperature was set at 250 ^oC.

The cloud and pour point were determined using a Mini Pour/Cloud Point tester model MPC-102A/102L from Tanaka Scientific Limited (Tokyo, Japan), using the L mode with detection intervals of 1 ^oC. The measurements were performed in triplicate and the average value is given.

The acid value of the starting material and products were determined using a slightly modified procedure reported by the National Cottonseed Products Association (Method number 28.029). The product (0.1 g) was weighed, dissolved in a mixture of diethyl ether and ethanol (50/50%-v/v) (20 mL), and then titrated with a 0.01 N KOH solution in ethanol using phenolphthalein as the indicator until a faint red colour appeared and persisted for at least 30 seconds.

The viscosity of JO and modification products was tested using a cone-and-plate rheometer AR1000-N from TA Instrument with a cone of 40 mm in diameter with a 2^o angle. The viscosity measurements were conducted at 40^oC for 900 s, with a shear rate of 10 s^{-1}.

Elemental analyses (C and H content) were carried out using an automated Euro EA3000 CHNS analyser with acetanilide as a calibration reference. All samples were analysed at least in duplicate and the average value is given.

3.2.3 Analytical data for the JO used in this study

Crude JO

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (m, -C***H***=C***H***-), 5.26 (m, OC***H***(CH2)2), 4.29 (dd, *J* = 11.8, 4.2 Hz, OCH(C***H***$_2$)$_2$), 4.14 (dd, *J* = 11.9, 5.9 Hz, OCH(C***H***$_2$)$_2$), 2.76 (t, *J* = 6.1 Hz, =CH-C***H***$_2$-CH=), 2.30 (t, *J* = 7.4 Hz, -C***H***$_2$COO-), 2.11 – 0.99 (m, -C***H***$_2$-), 0.87 (t, *J* = 5.0 Hz, -C***H***$_3$, end group). ^{13}C NMR (50 MHz, $CDCl_3$) δ 173.0 (–***C***OO–), 127.9–130.1 (***C***H=***C***H), 69.1 (–OCH(***C***H$_2$)$_2$), 62.2 (-***C***H$_2$COO-), 22.8–34.4 (-C***H***$_2$-), 14.3–14.4 (-***C***H$_3$, end group).

Elemental analysis, calculated: C 76.7%, H 11.9%. Found: C 77.3%, H 11.3%.

Acid value = 4.2 mg KOH/g oil.

3.2.4 Catalytic reactions

3.2.4.1 Trans-esterification of JO with methanol

The *trans*-esterification reaction of JO with methanol was performed using refined JO. The reaction was performed as follows: JO (10 g, 11.5 mmol of triglyceride), 25 wt% sodium methoxide in methanol (0.34 mL, 1.5 mmol of sodium methoxide), and methanol (2.8 mL, 69 mmol) were placed in a three-necked round bottom flask. The mixture was allowed to react under vigorous stirring at 65 ^{o}C for 3 hours. The resulting emulsion/dispersion was cooled to room temperature. The solids were removed by dropwise addition of water at room temperature without stirring. The liquid was collected and subjected to a centrifugation step to obtain a clear transparent phase. The water addition/centrifugation step was performed three times. The remaining methanol and water were separated from the esters at elevated temperatures under reduced pressure (T = 50 ^{o}C, 30 mbar) for 4 h. The methyl ester, **1**, was analysed by ^{1}H and ^{13}C NMR and elemental analyses.

Methyl esters of JO, **1**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (m, -C***H***=C***H***-), 3.63 (s, COOC***H***$_3$, methyl ester), 2.78 (t, *J* = 6.2 Hz, =CH-C***H***$_2$-CH=), 2.27 (t, *J* = 7.5 Hz, -C***H***$_2$COO-), 2.12 – 1.05 (m, -C***H***$_2$-), 0.83 (t, *J* = 7.0 Hz, -CH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ 174.2 (–***C***OO–), 130.0 – 127.9 (***C***H=***C***H), 51.5 (COO***C***H$_3$, methyl ester), 34.0 – 22.5 (m, -***C***H$_2$-), 14.0 (-***C***H$_3$, end group). Isolated yield: 9.97 g (95 wt% of theoretical yield).

Elemental analysis, calculated: C 77.0%, H 12.1%. Found: C 76.9%, H 12.1%.

3.2.4.2 (Trans-) esterification reactions of triolein, methyl oleate, and oleic acid with alcohols using metal triflate catalysts

Catalyst-screening studies were performed using triolein, methyl oleate, and oleic acid and the appropriate alcohol in glass ampoules. A representative example for methyl oleate and methanol is as follows: the ampoule was loaded with methyl oleate (0.15 g, 0.5 mmol), methanol (1.01 mL, 25 mmol), and catalyst (0.05 mmol). The ampoule was subsequently sealed using a torch and placed in a preheated oven

at a pre-determined temperature. After a pre-determined reaction time, the ampoule was taken from the oven and quenched by stepwise submersion in water at 90 and 20 ^{o}C. For safety reasons, particularly for reactions with gas phase formation, the ampoule was subsequently submerged in liquid nitrogen and opened. The liquid product was collected, washed with water, dried over $MgSO_4$, and analysed by ^{1}H and ^{13}C NMR and GC-MS.

For triolein, the ampoule was loaded with triolein (0.31 g, 0.35 mmol), methanol (0.7 mL, 17.5 mmol) and catalyst (0.035 mmol). The reactions were performed in a similar way as for methyl oleate.

The methyl esters yield, η_{methyl}, and the yield of the methyl esters containing methoxy group, $\eta_{methoxy}$, was based on integration of ^{1}H NMR spectra using the following equations:

$$\eta_{methyl}\,[mol\%] = \frac{\text{Peak area of } CH_3 \text{ methyl esters } (3.69 - 3.52\ ppm)}{\text{Peak area of } CH_3 \text{ end groups } (0.92 - 0.72\ ppm)} \times 100\%$$

$$\eta_{methoxy}\,[mol\%] = \frac{\text{Peak area of } CH_3 \text{ methoxy group } (3.31 - 3.22\ ppm)}{\text{Peak area of } CH_3 \text{ end groups } (0.92 - 0.72\ ppm)} \times 100\%$$

The yields of other alkyl esters, η_{alkyl}, and alkyl esters with alkoxy groups, η_{alkoxy}, were calculated using a similar method as defined above.

3.2.4.3 Preparative trans-esterification reactions of JO with higher alcohols

The preparative *trans*-esterification reactions of JO with higher alcohols were performed using unrefined JO in a microwave reactor. Typically, a glass vial was loaded with JO (5 g, 20.0 mmol of C=C), alcohol (500 mmol), and catalyst (2 mmol) and placed in the microwave reactor. The mixture was stirred using a double-cross magnetic stirrer (diameter ~ 1 cm) for 30 s and subsequently heated to the desired temperature in 2 minutes, and allowed to react for 1 h. The content was cooled to room temperature, washed three times with water and dried over $MgSO_4$. The remaining alcohol distilled of under reduced pressure, at a temperature slightly below the boiling temperature of the alcohol used. The product was analysed by ^{1}H and ^{13}C NMR and GC-MS.

Methoxy methyl esters of JO, **2**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (m, -C***H***=C***H***-), 3.65 (s, COOC***H***$_3$, methyl ester), 3.31 (s, CH-O-C***H***$_3$, methoxy), 3.10 (m, C***H***-O-CH_3, methoxy), 2.76 (t, *J* = 6.1 Hz, =CH-C***H***$_2$-CH=), 2.29 (t, *J* = 7.5 Hz, -C***H***$_2$COO-), 2.10 – 1.00 (m, -C***H***$_2$-), 0.87 (t, *J* = 7.1 Hz, -CH_3). ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.1 (***C***=O, lactone), 174.2 (-***C***OO-), 129.9 – 127.9 (***C***H=***C***H), 81.0 (-***C***H-, lactone), 56.3 (CH-O-***C***H_3, methoxy), 51.4 (COO***C***H_3, methyl ester), 33.9 – 22.6 (m, -***C***H_2-), 14.0 (-***C***H_3, end group). Isolated yield: 5.01 g (95 wt% of theoretical yield).

Elemental analysis, calculated: C 76.5%, H 12.1%. Found: C 76.5%, H 12.2%.

Ethoxylated ethyl esters of JO, **3**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (m, -C***H***=C***H***-), 4.10 (dd, *J* = 14.2, 7.1 Hz, COOC***H***$_2$CH$_3$, ethyl ester), 3.44 (m, CH-O-C***H***$_2$CH$_3$, ethoxy), 3.17 (m, C***H***-O-CH$_2$CH$_3$, ethoxy), 2.74 (t, *J* = 6.1 Hz, =CH-C***H***$_2$-CH=), 2.26 (t, *J* = 7.5 Hz, -C***H***$_2$COO-), 2.09 – 0.93 (m, -***C***H$_2$-), 0.85 (t, *J* = 5.2 Hz, C***H***$_3$). ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.3 (***C***=O, lactone), 173.8 (-***C***OO-), 130.2 – 127.7 (***C***H=***C***H), 79.3 (-***C***H-, lactone), 64.0 (CH-O-***C***H$_2$CH$_3$, ethoxy), 60.1 (COO***C***H$_2$CH$_3$, ethyl ester), 36.7 – 19.6 (-***C***H$_2$-), 15.6 (CH-O-CH$_2$***C***H$_3$, ethoxy), 14.4 – 13.9 (CH$_2$***C***H$_3$, end group and ethyl ester). Isolated yield: 5.23 g (94 wt% of theoretical yield).

Elemental analysis, calculated: C 77.0%, H 12.2%. Found: C 76.7%, H 12.2%.

Propoxylated propyl esters of JO, **4**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 – 5.17 (m, -C***H***=C***H***-), 3.95 (t, *J* = 6.7 Hz, COOC***H***$_2$CH$_2$CH$_3$, propyl ester), 3.47 – 3.27 (m, CH-O-C***H***$_2$CH$_2$CH$_3$, propoxy), 3.16 (m, C***H***-O-CH$_2$CH$_2$CH$_3$, propoxy), 2.74 (t, *J* = 6.2 Hz, =CH-C***H***$_2$-CH=), 2.37 – 2.16 (t, *J* = 7.5 Hz, -C***H***$_2$COO-), 2.10 – 1.03 (m, -***C***H$_2$-), 0.91 (t, *J* = 7.5 Hz, COOCH$_2$CH$_2$C***H***$_3$, propyl ester), 0.86 (m, C***H***$_3$, end group and propoxy). ^{13}C NMR (50 MHz, $CDCl_3$) δ 177.7 (***C***=O, lactone), 173.8 (-***C***OO-), 132.1 – 126.5 (***C***H=***C***H), 79.4 (-***C***H-, lactone), 70.6 (CH-O-***C***H$_2$CH$_2$CH$_3$, propoxy), 65.7 (COO***C***H$_2$CH$_2$CH$_3$, propyl ester), 35.8 – 20.5 (-***C***H$_2$-), 14.0 (***C***H$_3$, end group), 10.7 (CH-O-CH$_2$CH$_2$***C***H$_3$, propoxy), 10.3 (COOCH$_2$CH$_2$***C***H$_3$, propyl ester). Isolated yield: 5.52 g (95 wt% of theoretical yield).

Elemental analysis, calculated: C 77.5%, H 12.3%. Found: C 76.8%, H 12.3%.

Iso-propyl esters of JO, **5**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.23 (m, -C***H***=C***H***-), 4.99 (m, C***H***(CH$_3$)$_2$, isopropyl ester), 2.75 (t, *J* = 6.1 Hz, =CH-C***H***$_2$-CH=), 2.32 (t, *J* = 7.4 Hz, -C***H***$_2$COO-), 2.24 (t, *J* = 7.5 Hz, -C***H***$_2$COO-), 2.09 – 0.98 (m, -CH$_2$-), 0.86 (t, *J* = 5.4 Hz, C***H***$_3$, end group). ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.9 (***C***=O, lactone), 173.4 (-***C***OO-), 131.10 – 125.49 (***C***H=***C***H), 67.26 (***C***H(CH$_3$)$_2$, isopropyl ester), 35.1 – 22.2 (-***C***H$_2$-), 21.8 (CH(***C***H$_3$)$_2$, isopropyl ester), 14.0 (***C***H$_3$, end group). Isolated yield: 5.37 g (93 wt% of theoretical yield).

Elemental analysis, calculated: C 77.7%, H 12.3%. Found: C 76.9%, H 12.3%.

Iso-butoxylated *iso*-butyl esters of JO, **6**

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.12 (m, -C***H***=C***H***-), 3.75 (d, *J* = 6.8 Hz, COO-C***H***$_2$CH(CH$_3$)$_2$, isobutyl ester), 3.25 – 2.99 (m, C***H***-O-C***H***$_2$-CH-(CH$_3$)$_2$, isobutoxy), 2.74 (t, *J* = 6.2 Hz, =CH-C***H***$_2$-CH=), 2.28 (t, *J* = 7.6 Hz, -C***H***$_2$COO-), 2.00 (m, COO-CH$_2$C***H***(CH$_3$)$_2$, isobutyl ester) 1.95 – 1.03 (m, -C***H***$_2$-), 0.92 (s, COO-CH$_2$CH(C***H***$_3$)$_2$, isobutyl ester), 0.90 (s, COO-CH$_2$CH(C***H***$_3$)$_2$, isobutyl ester), 0.86 (t, ***J*** = 6.0 Hz, C***H***$_3$, end group). ^{13}C NMR (50 MHz, $CDCl_3$) δ 178.9 (***C***=O, lactone), 173.82 (-***C***OO-), 132.8

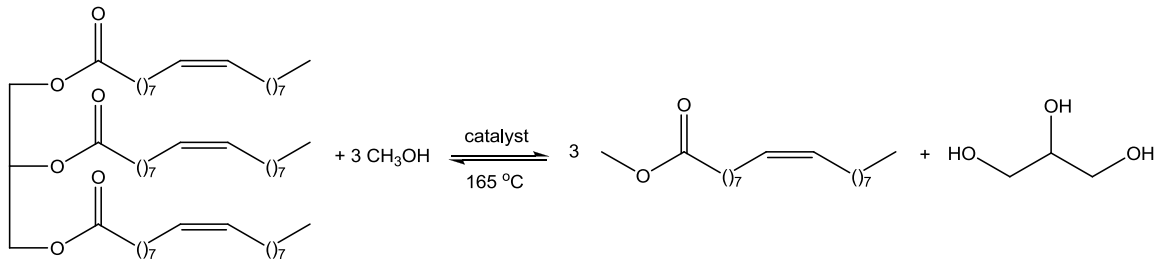
– 125.2 (-***C***H=***C***H-), 79.5 (-***C***H-, lactone), 75.9 (***C***H-O-CH_2-CH-$(CH_3)_2$, isobutoxy), 70.3 (COO-***C***H_2CH$(CH_3)_2$, isobutyl ester), 36.44 – 21.90 (-***C***H_2-), 19.5 (CH-O-CH_2-CH-(***C***$H_3)_2$, isobutoxy), 19.0 (COO-CH_2CH(***C***$H_3)_2$, isobutyl ester), 14.0 (***C***H_3, end group). Isolated yield: 5.64 g (94 wt% of theoretical yield).

Elemental analysis, calculated: C 77.5%, H 12.4%. Found: C 77.2%, H 12.4%.

3.3 Results and Discussion

3.3.1 Model studies on the *trans*-esterification of triolein with methanol using metal triflate catalysts

The potential of metal triflate catalysts for (*trans*)-esterification reactions with higher alcohols were assessed by performing model studies with a system consisting of triolein and methanol (165 °C, 1 h, methanol to triolein molar ratio of 50), see eq. 1.



(eq. 1)

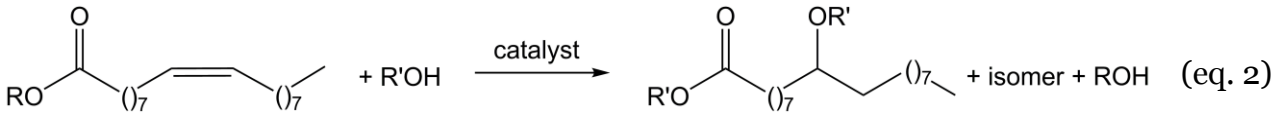
Six metal triflate catalysts were tested, *viz.* scandium, bismuth, zinc, aluminium, copper, and lanthanum triflate. In addition, aluminium chloride was used as well. The conversion of the triolein to methyl oleate was determined using ^{1}H NMR by monitoring the disappearance of characteristic peaks of the glycerol backbone at δ 5.26 and 4.0–4.35 ppm, and the appearance of a characteristic methyl ester peak at δ 3.6 ppm. The results of the catalyst-screening study are presented in Table 2.

Table 2 Results of the catalyst-screening study on the *trans*-esterification of triolein with methanol[a)]

Entry	Catalyst	Conversion (mol%)
1	$Sc(OTf)_3$	96
2	$Bi(OTf)_3$	98
3	$La(OTf)_3$	56
4	$Cu(OTf)_2$	92
5	$Al(OTf)_3$	99
6	$Zn(OTf)_2$	65
7	$AlCl_3.6H_2O$	7

[a)] The conversion is the average values of at least two experiments. Reaction conditions: 165 °C, conventional heating, 1 h, catalyst intake: 10 mol% to triolein, 50 fold molar excess of MeOH

$Sc(OTF)_3$, $Bi(OTf)_3$, and $Al(OTf)_3$ were the most active in the series and gave > 95 mol% conversion of the triolein, The other triflates are less active. The conversion using $AlCl_3$ was considerably lower than with $Al(OTf)_3$ (7 vs 99 mol%), indicating that the anion plays a role in the reaction mechanism and affects reaction rates. The major product is methyl oleate, as confirmed by ^1H and ^{13}C NMR spectra. However, ^1H NMR spectra of the products also showed a reduction of the intensity of the characteristic peaks of the C=C bonds at δ 5.29 ppm and the appearance of new peaks at δ 3.26 ppm (singlet) and δ 3.08 ppm (multiplet). Apparently, the C=C double bond is reactive under these conditions. A possible side reaction is methanol addition to the C=C bond to form an ether group (alkoxylation). Alkoxylation has also been reported by Madrigal [15] for the H_2SO_4-catalysed reaction of soybean oil with alcohols at 100-140 °C. Besides the esters, 18-31 mol% of the C=C was alkoxylated. In a more recent study, Moreau [16] and Pioch [17] described that (partly) methoxy methyl stearate was obtained when methyl oleate or oleic acid was reacted with methanol with dealuminated H-Y faujasites catalyst at 150-190 °C (see eq. 2).



(eq. 2)

R = H or CH_3

GC-MS analysis was applied to confirm the presence of methyl ether branches in the fatty acid chain. Two isomers were identified, i.e. methyl 9- and 10-methoxy octadecanoate with mass fragmentation patterns in line with those reported in the literature [16,18]. The extent of methoxylation was determined using ^1H NMR data and the results are shown in Fig. 2. Clearly, full conversion of the C=C bond is not observed and the maximum yield of methoxy group was less than 15% and depending on the metal triflate catalyst. Highest amounts of methoxy groups were observed for the $Bi(OTf)_3$ and $Al(OTf)_3$.

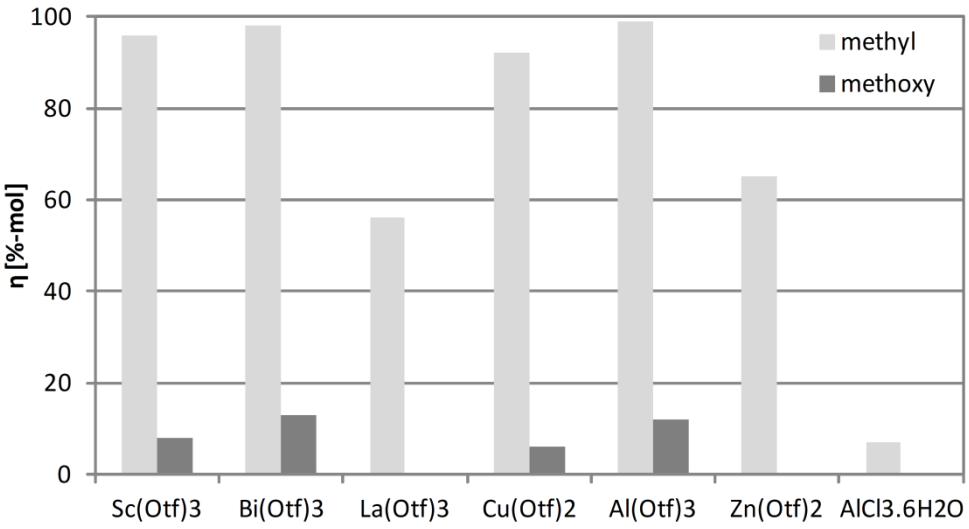


Fig. 2 Catalyst-screening study on the *trans*-esterification and alkoxylation of triolein with methanol. (165 °C, conventional heating, 1 h, 10 mol% catalyst intake on triolein, 50 fold molar excess of MeOH)

The introduction of branches on the fatty acid chain by an alkoxylation reaction may also have beneficial effect on the cold-flow properties of the product [15,19,20]. Therefore, the effect of process conditions on the $Al(OTf)_3$ catalysed alkoxylation with methanol were investigated with the primary objective to maximise the amount of methoxy branches. For this purpose, the extent of methoxylation was studied by performing reactions using methyl oleate and methanol as model compounds. The reaction time, molar excess of methanol to methyl oleate and catalyst loading were varied. The yield of the methoxy groups versus time at different molar excesses of methanol are shown at Fig. 3.

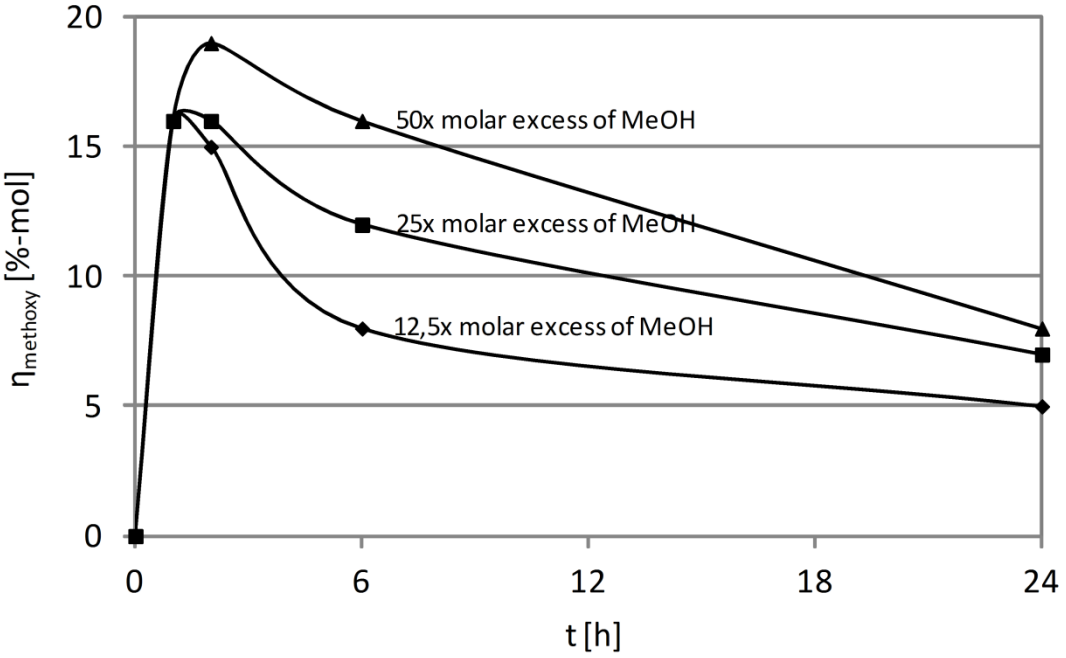
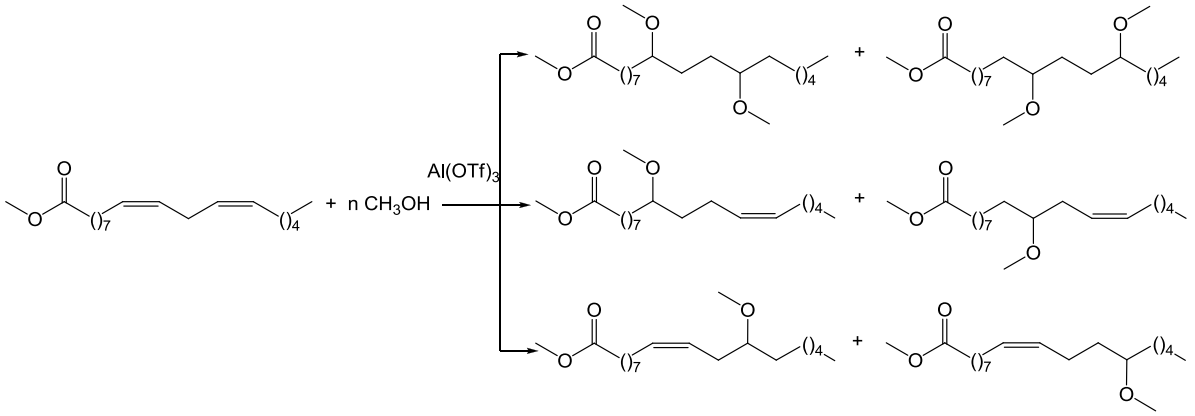


Fig. 3 Methoxylation of C=C bonds versus time at different methanol ratios for the alkoxylation of methyl oleate with methanol using $Al(OTf)_3$ (trendlines are for illustrative purpose only, 165 °C, conventional heating)

The yield of methoxy groups versus time shows a clear maximum at about 2-3 h reaction time. The maximum yield was about 18 mol% for the highest methanol to methyl oleate ratio. At prolonged reaction times, the yields of the methoxy product are lowered to about 5 mol%. This finding is not in agreement with the methoxylation of methyl oleate using solid dealuminated Y faujasites catalysts [16,17]. Here, the yield of methoxy products remained constant at a level between 40 and 50% after prolonged reaction times, indicative for an equilibrium reaction. A possible explanation is the occurrence of other methanol consuming reactions (e.g. etherification, *vide infra*) catalysed by the metal triflates, driving the equilibrium to the side of the starting material. Further detailed studies will be required to draw definite conclusions.

Higher catalyst intakes also did not lead to higher yields of the methoxy products. Using a 50 mol% catalyst loading and a 50 times molar excess MeOH, 16 mol% methoxy product after 1 h reaction time was obtained, which is similar to the value obtained at lower intakes. After 24 h, the amount was reduced to 5 mol%.

The alkoxylation reaction with methanol was also performed with methyl linoleate instead of methyl oleate. With $Al(OTf)_3$ at 165 ^oC, partial methoxylation of the C=C bonds occurred and an isomeric mixture of mono- and di-methoxy methyl stearate was obtained (Scheme 1). The presence of these compounds was confirmed by GC-MS analyses.

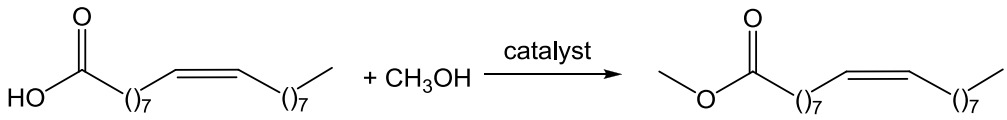


Scheme 1 Methoxylation of methyl linoleate using $Al(OTf)_3$ catalyst

Clear GC peaks with characteristic mass fragmentation patterns in line with literature data [21] were observed for methyl 9(10),12(13)-dimethoxyoctadecanoate, methyl 9(10)-methoxy-12(13)-octadecenoate, and methyl 12(13)-methoxy-9(10)-octadecenoate.

3.3.2 Model studies on the esterification of oleic acid with methanol using metal triflate catalysts

A second series of catalytic reactions using metal triflate catalysts were carried out with a free fatty acid (oleic acid) instead of the triolein (eq. 3).

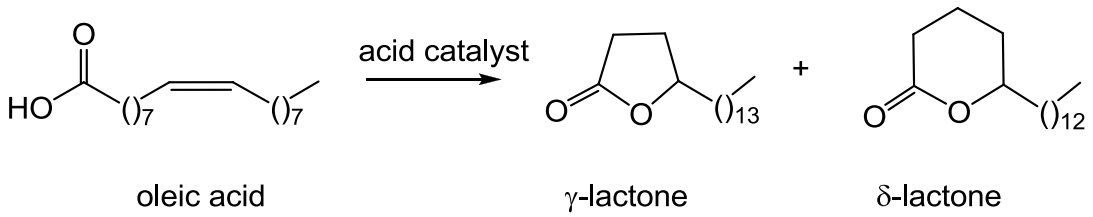


(eq. 3)

The reactions were performed at two temperatures (135 and 165 ^oC). ^1H NMR spectra of the reaction product showed quantitative conversion of the free fatty acid to the methyl ester at both temperatures using all catalysts. We selected $Al(OTf)_3$ for further studies as it is very active, non-toxic, and never been applied before in existing literatures. The conversions of the *trans*-esterification reaction of triolein with methanol (*vide supra*) were not quantitative at 165 ^oC. Apparently, the esterification reaction is much faster than the *trans*-esterification reaction at these conditions, which is in line with literature data in the (*trans*-) esterification of triolein and oleic acid with $Sc(OTf)_3$ and $Bi(OTf)_3$ [11]. Alkoxylation also occurred,

with yields in the range as observed for the *trans*-esterification reaction of triolein with methanol.

^{13}C NMR spectra of the product show, next to the characteristic peak of the methoxy ester group at δ 56.3 ppm, small peaks at δ 177.2 and δ 80.9 ppm. A possible side reaction is the isomerisation – lactonisation of free fatty acids (eq. 4).



Characteristic peaks of the lactones were not clearly observed in the ^{1}H NMR spectra of the products due to overlap with other peaks, and this hampers quantification of the amount of lactones formed. Based on available ^{13}C NMR data [22], the peaks at δ 177.2 and δ 80.9 ppm are indicative for the formation of the γ-lactone instead of the δ-lactone.

The lactonisation of unsaturated fatty acids using metal triflates has been reported in the paper of Gooβen and co-workers [23], reported that AgOTf, $Bi(OTF)_3$, $In(OTf)_2$, and $Cu(OTf)_2$ catalysts are active catalysts for the isomerisation-lactonisation of 10-undecenoic acid to the corresponding γ-lactone. At 160 ^{o}C, using 5 mol% of the catalyst, highest yield (50 mol%) was obtained using the AgOTf catalyst. The isomerisation-lactonisation of internal unsaturated fatty acids with 9, 13, and 18 carbon chains using AgOTf at 130 ^{o}C gave γ-lactones in isolated yields between 51 – 72 mol% (24 h, chlorobenzene) [23]. Cermak and Isbell [22] reviewed methods for the isomerisation – lactonisation of unsaturated fatty acids to give δ- and γ-lactone using sulphuric acid in stoichiometric or super stoichiometric amounts. At low temperatures (< 20 ^{o}C), the major product were δ-lactones, while γ-lactones were the major product at moderate temperatures (50–150 ^{o}C).

3.3.3 Model studies on the *trans*-esterification of methyl oleate with higher alcohols using $Al(OTf)_3$

The *trans*-esterification of methyl oleate with higher alcohols (EtOH, n-PrOH, i-PrOH, i-BuOH, t-BuOH) was studied with $Al(OTf)_3$, one of the most active catalyst for the reaction of triolein with methanol (Fig. 2). For all alcohols, except t-BuOH, quantitative *trans*-esterification and the formation of the ester of the higher alcohol was observed in 1 h at 165 ^{o}C. The alkoxylation reaction of the C=C bond in the fatty ester also occurred for EtOH, n-PrOH, and iBuOH, though the maximum yield of the alkoxylated ester was again low (< 10%), see Fig. 4 for details. Alkoxylation was not observed for i-PrOH, the only secondary alcohol in the series, presumably for steric/electronic reasons. Similar results were reported for the *trans*-esterification

and alkoxylation reaction of soybean oil with i-PrOH using H_2SO_4 as the catalyst (140 ^oC, 19h) [15].

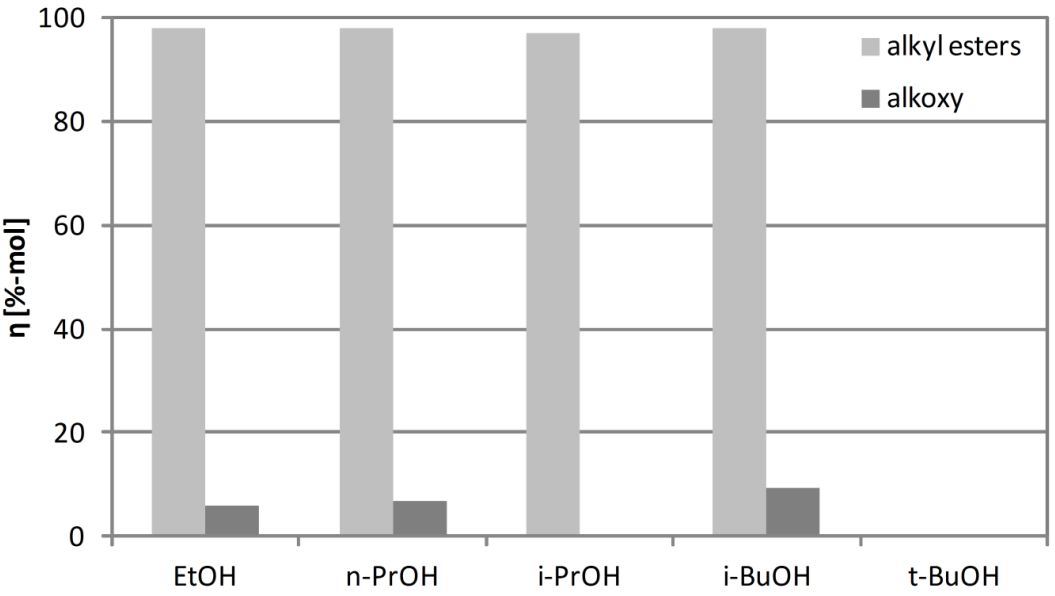
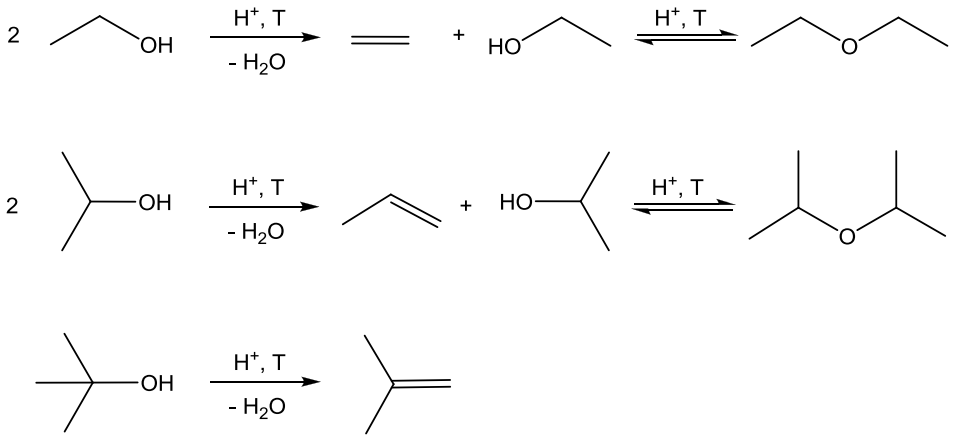


Fig. 4 Yields of esters and alkoxylated products for the reaction of methyl oleate with higher alcohols using $Al(OTf)_3$ as the catalyst (10 mol% catalyst, 50 fold molar excess of alcohol, 185 ^oC, conventional heating, 1 h).

It is well known that the rates of *trans*-esterification reactions are highly depending on the molecular structure of the alcohols. Primary alcohols are the most reactive, followed by secondary alcohol, and the least reactive are tertiary alcohols [24]. As such, it is also not surprising that t-BuOH was not reactive under these reaction conditions.

Possible byproducts when using higher alcohols are olefins and ethers by dehydration/addition reaction (Scheme 2) [25].



Scheme 2 Possible reaction pathway of dehydration and etherification of primary, secondary, and tertiary alcohols [25,26,27]

To assess the occurrence of these reactions, i-PrOH and the $Al(OTf)_3$ catalyst were allowed to react at standard reaction conditions (185 ^{0}C, 1 h). The gaseous products were collected and analysed using GC-MS. Both propylene and di-isopropyl ether were detected, proof for the occurrence of dehydration and etherification reaction.

3.3.4 *Trans*-esterification reactions of JO with alcohols using $Al(OTf)_3$ as the catalyst

3.3.4.1 JO characterisation

The fatty acid composition of the JO used for this study was determined using GC-MS and the results are given in Table 3.

Table 3 Fatty acid composition of the crude JO used in this study

Fatty acid		**This study**		**Literature** [28]
		wt% (GC-FID)	**mol%**	**wt%**
Palmitoleic acid	C16:1	0.9	1.0	0 – 1.3
Palmitic acid	C16:0	11.7	12.7	14.1 – 15.3
Linoleic acid	C18:2	43.8	43.5	29.0 – 44.2
Oleic acid	C18:1	38.2	37.6	34.3 – 45.8
Stearic acid	C18:0	5.3	5.2	3.7 – 9.8
Total unsaturated acids		82.9	82.1	63.4 – 91.3

The composition of JO used in this study is close from that reported in literature with a very slight difference in the amount of palmitic acid. The total amount of unsaturated fatty acids in the JO used in this study is 82.9 wt%. The acid value was determined by titration and found to be 4.2 mg KOH/g oil, corresponding with a FFA content of 2.1 wt% (as oleic acid), indicating that the oil contains significant amounts of free fatty acids.

3.3.4.2 Preparative reactions of JO with higher alcohols

Preparative reactions of JO with methanol and various higher alcohols (EtOH, n-PrOH, i-PrOH, i-BuOH, t-BuOH) using $Al(OTf)_3$ were performed in a microwave reactor (T = 165 or 185 ^{0}C, catalyst intake of 10 mol%, 25 fold molar excess of alcohol, 1 h). After reactions, the esters were obtained as yellow liquids in > 93 wt% isolated yield and analysed by ^{1}H and ^{13}C NMR and elemental analyses. An overview of the results is given in Table 4. *Tert*-butanol was not reactive, a result in line with the model component study. The reaction with i-PrOH was carried out at 135 ^{0}C. At higher temperatures, the pressure exceeded the maximum pressure in the microwave

reactor due to the formation of gas phase component like propylene by the catalytic decomposition of i-PrOH (*vide supra*).

Table 4 Overview of results for the reaction of JO with higher alcohols using $Al(OTf)_3$ as the catalyst[a)]

Alcohol	Compound	η_{alkyl} [mol%]	η_{alkoxy} [mol%]	Final acid value [mg KOH/g oil]
MeOH[b)]	**2**	98	11	0.10
EtOH[c)]	**3**	98	9	0.11
n-PrOH[c)]	**4**	98	8	0.11
i-PrOH[d)]	**5**	97	0	0.13
i-BuOH[c)]	**6**	98	21	0.12
t-BuOH[e)]	-	0	0	n.d.[f)]

[a)]Values are average values of two duplicate experiments. Reaction conditions: 25x molar excess of alcohol, catalyst loading: 10 mol% to C=C; [b)]at 165 °C; [c)]at 185 °C; [d)]at 145 °C due to pressure safety limit of reactor (21 bars); [e)]at 135 °C due to pressure safety limit of reactor (21 bars); [f)]not determined

Table 5 Summary of characteristic peaks for products of the reaction of JO with higher alcohols using $Al(OTf)_3$ as the catalyst

Alcohol	Ester group (ppm)		Alkoxy group (ppm)		Lactone group (ppm)
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR	^{13}C NMR
MeOH	3.65 (C***H***$_3$)	51.4 (***C***H$_3$)	3.31 (C***H***$_3$), 3.10 (C***H***)	56.3 (***C***H$_3$)	178.3 (C=O), 81.0 (***C***H)
EtOH	4.10 (C***H***$_2$)	60.1 (***C***H$_2$)	3.44 (C***H***$_2$), 3.17 (C***H***)	64.0 (***C***H$_2$)	178.3 (C=O), 79.3 (***C***H)
n-PrOH	3.95 (OC***H***$_2$), 0.91 (C***H***$_3$)	65.7 (O***C***H$_2$), 10.3 (***C***H$_3$)	3.47-3.27 (OC***H***$_2$), 3.16 (C***H***O), 0.86 (C***H***$_3$),	70.6 (O***C***H$_2$), 10.7 (***C***H$_3$)	177.7 (C=O), 79.4 (***C***H)
i-PrOH	4.99 (C***H***)	67.3 (***C***H), 21.8 (***C***H$_3$)$_2$	-	-	178.9 (C=O)
i-BuOH	3.75 (OC***H***$_2$), 2.00 (C***H***), 0.92 and 0.90 (C***H***$_3$)$_2$	70.3 (O***C***H$_2$), 19.0 (***C***H$_3$)$_2$	3.25-2.99 (C***H***OC***H***$_2$)	75.9 (***C***HOCH$_2$), 19.5 (***C***H$_3$)	176.9 (C=O), 79.5 (CH),

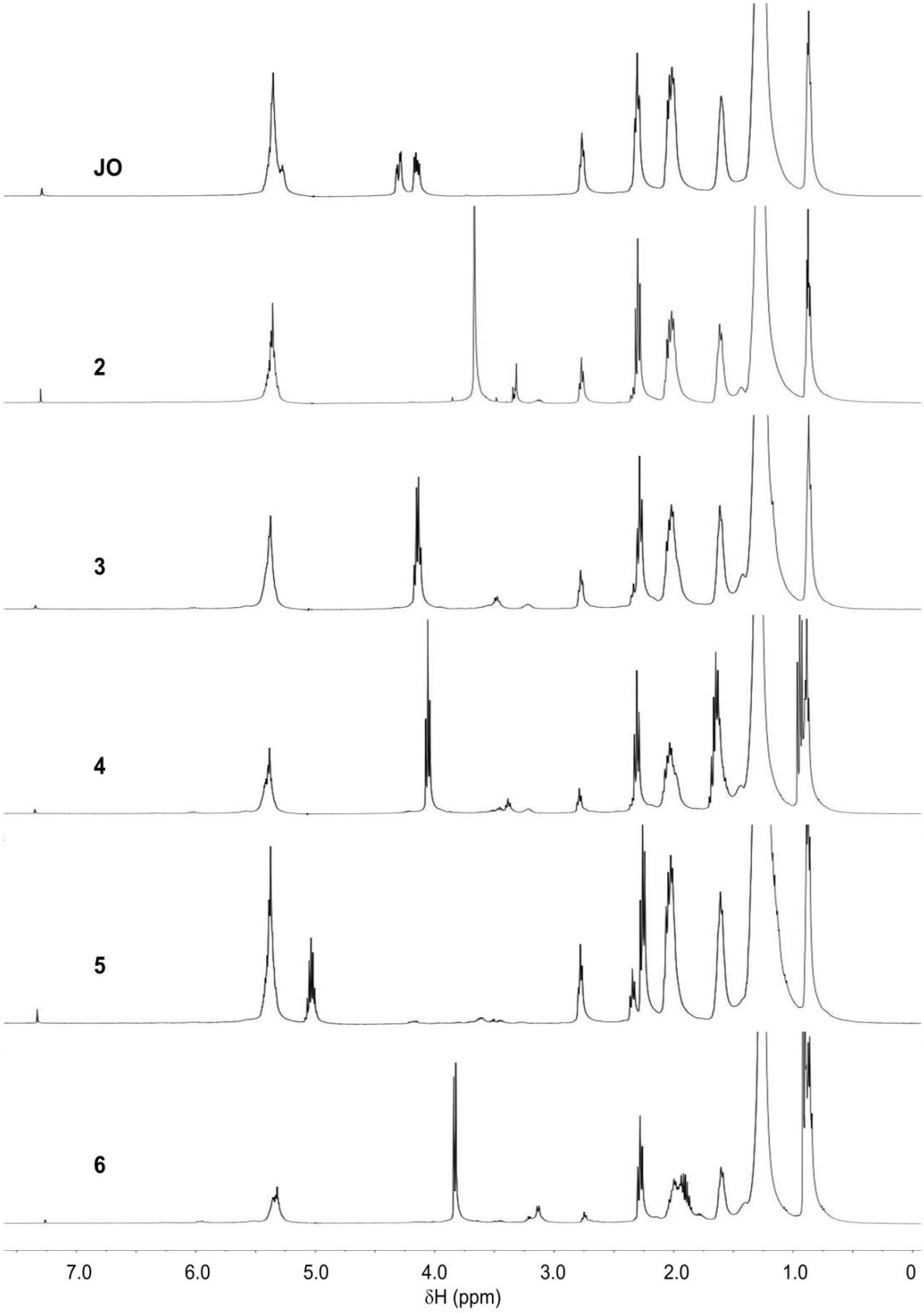


Fig. 5 ^{1}H NMR spectra of JO and derivatives

The FFA value of the products ranged between 0.05-0.06 (wt%) and this value is considerably lower than the JO feed (2.1 wt%). This indicates that both *trans*-esterification of the triglycerides and esterification of the free fatty acids occurred, in line with the model component studies.

^{1}H NMR spectra of the products (Fig. 5) and ^{13}C NMR show the presence of the ester and alkoxy groups (Table 5). The extent of alkoxylation was in line with the model component studies, and the highest yield was obtained by i-BuOH (Table 4). In addition, small amounts of γ-lactones were detected in ^{13}C NMR spectra, though could not be quantified.

3.3.4.3 Properties of the JO derivatives

Relevant physical properties of the ester derivatives with an emphasis on cold flow properties were determined. The viscosity of the JO feed and the higher alcohol esters derived thereof are provided in Table 6. As expected, the viscosity of the esters is considerably lower than the original JO. The ester substituent affects the viscosity and the viscosity increases with the number of carbon atoms in the alcohol, viz 5.76 for MeOH to 8.26 mPa.s for i-BuOH. The synthetic methodology described in the paper leads to partial alkoxylation of the C=C of the fatty acids chains. To check whether these branches affect the viscosity of the product, the viscosity of the JO methyl ester (**2**) was compared with a JO methyl ester (**1**) prepared by a standard base catalysed *trans*-esterification of JO with methanol. The viscosity of **2** is a factor 1.3 higher than that of **1**, an indication that the additional methoxy branches lead to higher viscosities.

Table 6 Dynamic viscosity of JO and derivatives at 40 ^{o}C

Compound	Alcohol	Viscosity [x 10^{-3} Pa.s]
JO	-	34.06
methyl esters of JO (**1**) [a)]	MeOH	4.47
methoxy methyl esters of JO (**2**) [b)]	MeOH	5.76
ethoxylated ethyl esters of JO (**3**)	EtOH	6.93
propoxylated propyl esters of JO (**4**)	n-PrOH	7.66
iso-propyl esters of JO (**5**)	i-PrOH	8.20
iso-butoxylated *iso*-butyl esters of JO (**6**)	i-BuOH	8.26

[a)]Prepared using a standard base catalysed *trans*-esterification of JO with methanol
[b)]Prepared using the synthetic methodology described in this paper; product contains -OMe groups in fatty acid chain

The cold flow properties of the JO and higher alcohol derivatives were determined and the results are given in Fig. 6. The CP and PP of JO were -2 and -3 ^{o}C, respectively, and these values are in line with literature data (CP of 2 ^{o}C [29] and

PP of -3 °C [29,30]). The PP is in the expected range for plant oils, see Fig. 1, with higher levels of unsaturation leading to lower PP values.

The CP and PP of the methyl esters of JO, **1**, were 0 and 1 °C, respectively. These values are slightly higher than for JO. Apparently, the *trans*-esterification reaction with methanol does not have a significant effect on cold flow properties, though considerably lowers the viscosity (*vide supra*).

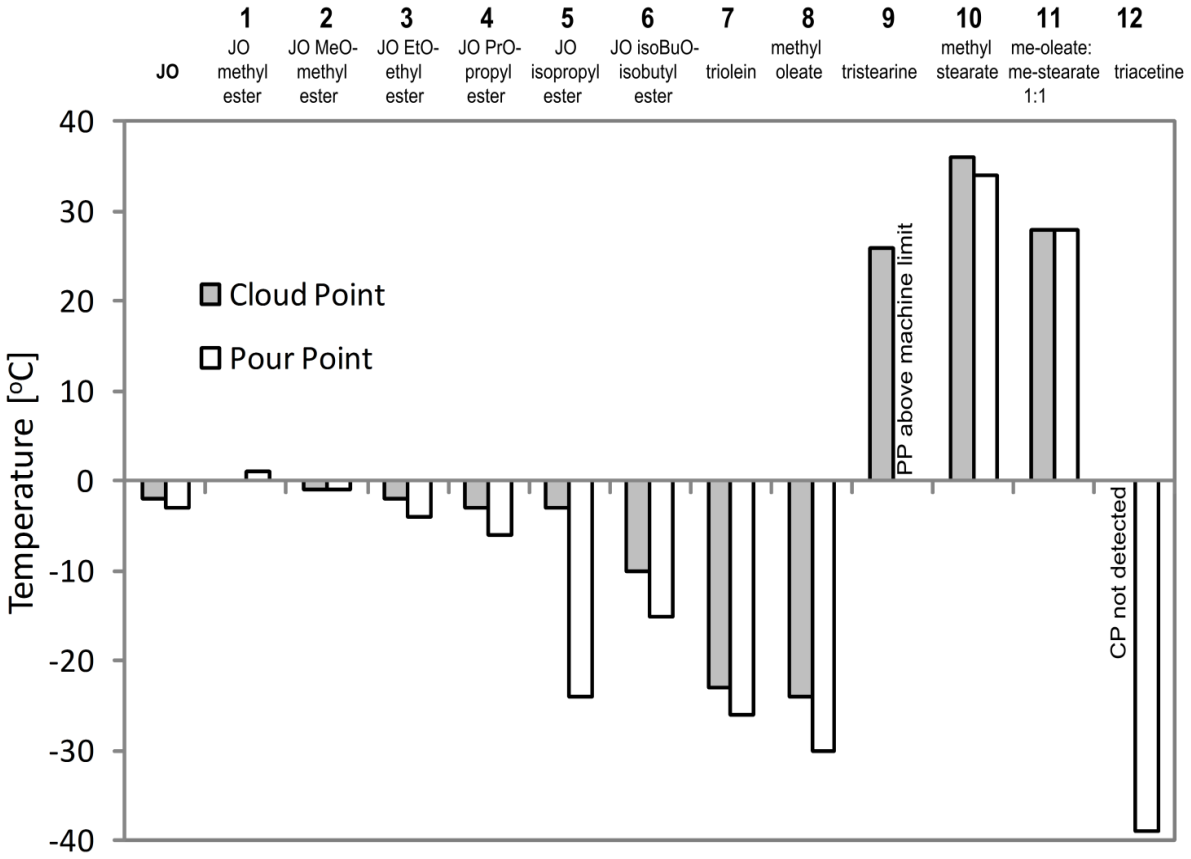


Fig. 6 Cold flow properties of JO and derivatives

Table 7 Cold flow properties of PPO and their alkyl esters

	Plant	CP / PP values		Mol ratio unsaturated/ saturated chains	Average chain length	Ref
		Oil	Methyl ester			
1	Castor	4.0/-15.0	7.0/-25.0	97.0/3.0	18.0	
2	Pumpkin	3.0/-8.0	5.0/-12.0	79.3/20.7	17.8	[31]
3	Groundnut	8.0/-3.0	10.0/-6.0	69.4/30.5	18.2	
4	Rapeseed	-3.9/-31.7	-2.0/-9.0	94.0/6.0	17.9	
5	Soybean	-3.9/-12.2	2.0/-1.0	89.5/10.5	17.9	[32]
6	Sunflower	7.2/-15.0	0.0/-4.0	92.0/8.0	17.9	

PP and CP values for several plant oils and methyl esters derived thereof are given in Table 7. It shows that in general the CP is increased upon *trans*-esterification while an opposite pattern is observed for the PP.

For comparison, the PP and CP of pure triolein (**7**) and methyl oleate (**8**) were detemined. The CP/PP of triolein and methyl oleate are in the same range, -23/-26 and -24/-30 ^{o}C, respectively. The values for methyl oleate are much lower than for the JO methoxy methyl esters (**2**), likely caused by the saturated fatty ester fraction in the JO methoxy methyl esters, which is known to most prone to crystallisation. Support for this statement was obtained by measuring the PP and CP of methyl stearate (**10**) and mixtures of methyl stearate and methyl oleate (1:1 by weight, **11**). Methyl oleate has a CP and PP of -24 and -30 ^{o}C, while the values for methyl stearate are much higher, 36 and 34 ^{o}C, respectively (see Fig. 6). The mixture **11**, resulted in a CP and PP of 28 ^{o}C, close to those of methyl stearate. Thus, the cold flow properties of fatty acid methyl esters are affected heavily by the amount of saturated fatty acid chains.

The synthetic methodology reported in this paper for the synthesis of the methyl ester of JO results, besides the introduction of ester groups, also to the introduction of methoxy groups (-OMe) on the fatty acid chain by methoxylation of the C=C. The effect of these additional branches on the PP and CP was probed by comparing the values with that of the JO methyl esters (**1**) prepared using standard base catalysed methodology. The PP and CP of the methyl ester with -OMe ether groups (**2**) are 1-2 ^{o}C lower than the methyl ester without these additional branches. Thus, the effect is limited, which could be due to the relatively low amounts of ether methoxy groups (*vide supra*).

A number of JO esters with different alcohols was prepared and this allows an assessment of the effect of the size of the JO ester group on cold flow properties. When considering the primary alcohols in the series (MeOH, EtOH, n-PrOH, i-BuOH), the C4 alcohol in the series (**6**) gave the lowest PP and CP, viz -10, and -15 ^{o}C versus -1 and -1 ^{o}C for the methyl ester **2**. Thus the cold flow properties are considerably improved by using higher alcohols for the esterification reaction. The lowest values for the CP and PP were obtained for the secondary alcohols in the series (i-PrOH, **5**), -3 and -24 ^{o}C, respectively. Thus, not only the number of carbon atoms in the alcohol but also the position of the substituents on the ester group plays a role .

3.4 Conclusions

Metal triflates were shown to be active catalysts for the *trans*-esterification of Jatropha oil and the esterification of the FFA in the oil with various alcohols. Besides *trans*-esterification, partial alkoxylation of the carbon-carbon double bonds, and to a lesser extent, isomerisation-γ-lactonisation of the free unsaturated fatty acids in the oil occurred. Aluminium triflate was found to be the most active catalyst and this finding is an absolute novelty of this paper. Quantitative yields were obtained for the *trans*-esterification reaction when using primary and secondary alcohols, whereas a tertiary alcohol like t-BuOH was not reactive. Alkoxylation of the carbon-carbon double bonds was accomplished exclusively for primary alcohols, with higher

alcohols being more reactive. Cold flow properties of the Jatropha oil derivatives were determined and best results were obtained for the *iso*-propyl esters of JO, with CP and PP values of -3 and -24 ^{o}C, respectively.

3.5 List of abbreviations

JO = *Jatropha curcas* L. oil
1 = methyl esters of JO
2 = methoxy methyl esters of JO
3 = ethoxylated ethyl esters of JO
4 = propoxylated propyl esters of JO
5 = *iso*-propyl esters of JO
6 = *iso*-butoxylated *iso*-butyl esters of JO
7 = triolein
8 = methyl oleate
9 = tristearine
10 = methyl stearate
11 = mixture of methyl oleate: stearate= 1:1 (wt/wt)
12 = triacetine (triacylglycerol of acetic acid)
CP = cloud point
PP = pour point
C=C = carbon-carbon double bonds
MeOH = methanol
EtOH = ethanol
n-PrOH = *n*-propanol
i-PrOH = *iso*-propanol
i-BuOH = *iso*-butanol
t-BuOH = *tert*-butanol

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Chapter 4

Exploratory studies on the catalytic oxidation of levulinic acid to succinic acid

Summary

An exploratory study on the catalytic oxidation of levulinic acid (LA) to succinic acid (SA) is reported using a wide range of homogeneous catalysts. Sulphuric acid in combination with hydrogen peroxide in acetonitrile was found to be the best catalytic system giving a SA selectivity of 73 mol% at 55 mol% LA conversion (80 ^{o}C, 0.5 M H_2SO_4 and a 5 fold excess of aqueous H_2O_2). Besides SA, malonic acid (MA), acetic acid (AA), and formic acid (FA) were formed as well. The catalytic system was also explored for the oxidation of furfural and other relevant abundantly available biopolymers (starch, cellulose), their hydrolysed monomers (D-glucose and xylose) and a lignocellulosic biomass source in the form of *Jatropha curcas* L. (JCL) seed shells. For furfural, a SA yield of about 40 mol% at full furfural conversion was obtained in water (105 ^{o}C). A two-step approach was applied for glucose, cellulose, xylose, and starch, involving the acid catalysed hydrolyses in water to LA and/or furfural followed by the subsequent oxidation using hydrogen peroxide. Highest SA yield (23 mol% based on LA in hydrolysate, 10 mol% based on substrate) were obtained for D-glucose. For JCL seeds, the SA yield was 25 mol% (based on LA in hydrolysate, or 6 mol% based on the C6 sugar content in the feed).

Keywords: bio-succinic acid, levulinic acid, oxidative cleavage, biomass

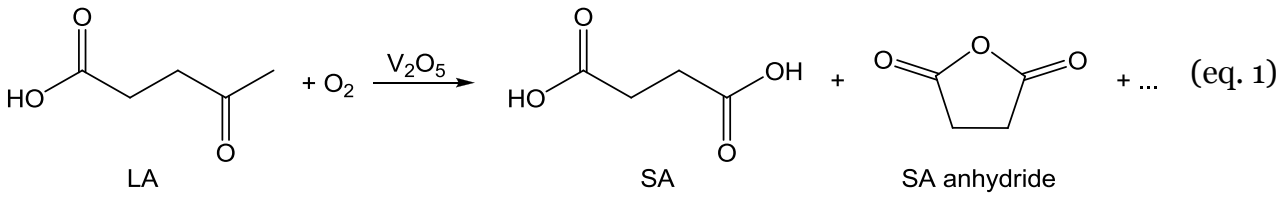
4.1 Introduction

Succinic acid (1,4-butanedioic acid, SA) is a commodity chemical with a limited global market size of 20 – 30 kton/year [1-4]. However, commercial prospects are high and the market size is projected to increase to 180 kton/year by 2015 [4], with further extension to 270 kt/year [5]. SA is currently produced mainly by the catalytic oxidation of butane to maleic anhydride over vanadium phosphorus oxide catalyst [6,7] followed by hydrogenation to succinic acid anhydride. Other catalytic processes include oxidation of isomerised kerosene in the presence of aqueous solution of transition metal carboxylates, particularly cobalt (II) [8], as well as catalytic hydrogenations of maleic acid or fumaric acid [2,9].

The development of green routes to SA using renewable feedstocks is high on the global research agenda [10]. Biotechnological processes involving fermentation of glucose, xylose, glycerol, cane molasses, whey, lignocellulosic carbohydrates, and even with higher carbohydrates such as wheat and corn [2] have been performed. Some of these processes are now close to full scale commercialisation. At least five groups/joint ventures have recently started bio-based SA production, BioAmber (United States) - Dupont (France) [11], Myriant Technologies (US) – PTT Chemical (Thailand) [12], BASF (Germany) – CSM (Netherlands), DSM (Netherlands) - Roquette Frères (France) [13], and very recently, Mitsubishi Chemical Company – Ajinomoto (Japan) [4]. So far, a productivity of up to 3.9 g SA/(L.h) has been reported, with SA yields of up to 0.70 g/g of glucose [14].

An alternative, non-fermentative route to SA involves the use of levulinic acid (4-oxo-pentanoic acid, LA) as the precursor. LA may be obtained in yields up to 20 wt% from lignocellulosic biomass [15] and is considered a very attractive biomass derived platform chemical with high application potential. LA production has been demonstrated at semi-commercial scale (Bio-fine). The price for LA has decreased from approximately 8.8-13 $/kg in 2005 to 3.2 $/kg at 2010 [16], and predicted to be as low as 0.08-0.22 $/kg in the future, depending on the scale of operation [17].

Literature on the oxidation of LA to SA is scarce and most publications are from before 1956. Oxidation of LA vapour over a V_2O_5 catalyst at 275 – 400 ^oC is to the best of our knowledge the only known catalytic chemical route for LA oxidation to give reasonable yield of SA and its anhydride (83 wt%, eq. 1) [18]. Another example is the $CuSO_4$ – catalysed oxidation of LA with hydrogen peroxide to SA and acetone, however, the former was only produced in very low yields [19]. The oxidation of a LA derivative, 5-chloro-LA, using nitric acid to SA has also been reported, though yields are not provided [20].

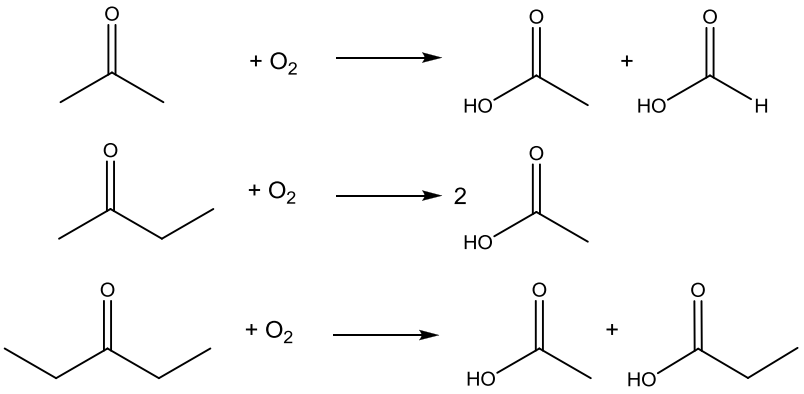


(eq. 1)

Therefore, there is a clear incentive to develop catalytic chemistry for the low temperature oxidation of LA to SA. This will require the selective oxidation of the methyl group adjacent to the carbonyl group instead of the CH_2 group. Oxidative cleavage of ketones is well known using stoichiometric oxidants [21-25]. An example is the industrial production of adipic acid from cyclohexanone using nitric acid as the oxidant [26]. This process has also been performed catalytically by using NH_4VO_3 or $Cu(NO_3)_2$ as catalyst [27].

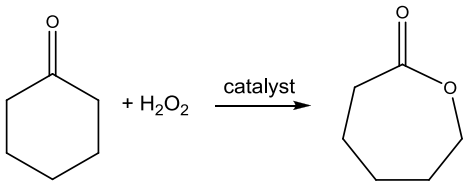
The oxidative cleavage of cyclic and aliphatic ketones has also been performed catalytically using molecular oxygen. Examples are the use of heteropolyacids [21], supported gold catalyst [28], sodium methoxide, sodium hydroxide, and potassium hydroxide [29], as well as homogeneous metal catalysts based on palladium, copper, iron, cerium, cobalt, and manganese [21], rhodium, iridium, platinum [30], rhenium [31,32], and vanadium [21,33]. The homogeneous metal catalysts were effective for the oxidative cleavage of aliphatic, open chain ketones. Other catalytic systems for the oxidation of aliphatic open chain ketones include acidic metal oxide catalysts such as V_2O_5, MoO_3, WO_3, U_3O_8, Cr_2O_3, V_2O_5-P_2O_5 [34-37], TiO_2 [38], as well as with manganese sulphate catalyst [39] and activated carbon [40]. The oxidative cleavage with oxygen is proposed to involve hydroperoxy intermediates [40].

The regioselectivity of the reaction depends on the substitution pattern of the carbon atoms adjacent to the carbonyl group, the order being reported as tertiary carbon > secondary carbon >> primary carbon (Scheme 1). Non-substituted and α-substituted cyclic ketones also follow this rule [28,29].



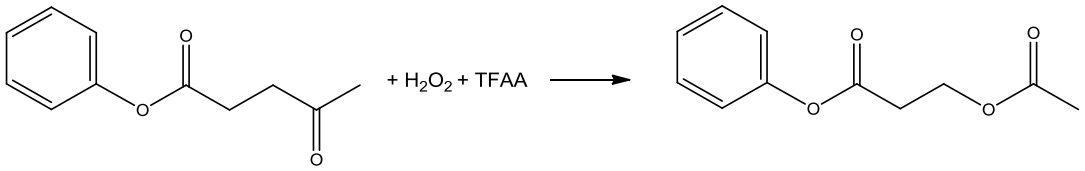
Scheme 1 Oxidative cleavage of acetone, butanone, and 3-pentanone with molecular oxygen [30]

Hydrogen peroxide is also widely used as the oxidant and a well-known example is the Baeyer-Villiger oxidation reaction (BVO, see eq. 2 for a representative example) [41].



(eq. 2)

The BVO may be performed stoichiometrically as well as catalytically. The selectivity of the reaction is substrate specific. For instance, the BVO of benzyl levulinate with hydrogen peroxide [42] gave benzyl 3-acetoxypropionate as the sole product in 63 wt% yield (eq 3).



(eq. 3)

This example illustrates that the methyl group adjacent to the carbonyl group is less reactive than the CH_2 group, indicating that this method seems less appropriate for the conversion of LA to SA. However, two catalytic BVO systems using methyltrioxorhenium [43] and sodium hydroxide [44] have been reported to proceed with unusual product regio-chemistry for cyclic and bridged bicyclic ketones and as such are of interest for this investigation. In addition, novel BVO systems have been introduced recently using Brönsted and Lewis acid catalysts to oxidise cyclic ketones with hydrogen peroxide in alcoholic solvent to the corresponding dicarboxylic acid esters [45-47]. Examples of catalysts are H_2SO_4, $BF_3.Et_2O$, and HBF_4.

In summary, selective catalytic routes at mild conditions for the oxidation of LA to SA are lacking. We here report an exploratory study on the oxidative cleavage of LA to SA at such conditions using hydrogen peroxide besides oxygen as the main oxidant.

4.2. Experimental section

4.2.1 Materials

Levulinic acid (98%), succinic acid (≥99.0%), malonic acid (99%), copper (II) oxide (powder, <5μm, 97%), Copper(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29*H*,31*H*-phthalocyanine (F_{14}CuPc, dye content 80%), sulphuric acid (95-98%), n-butanol (99.9%), bromine (reagent grade), 1,4,7-trimethyl-1,4,7-triazacyclononane (97%), manganese(III) acetate dihydrate (97%), sodium acetate (≥99.0%), ethanol (≥99.5%), potassium hexafluorophosphate (98%), triethylamine

(≥99.5%), $(PPh_3)_2PtO_2$, basic Al_2O_3, hydroiodic acid (57 wt. % in H_2O, distilled, stabilized, 99.95%), iodine (*ReagentPlus*®, ≥99.8% (titration)), urea (*ReagentPlus*®, ≥99.5%, pellets), sodium bicarbonate (ACS reagent), sodium tetrachloroplatinate (II) hydrate, N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with trimethylchlorosilane (99.0%, 1% TMCS), were obtained from Sigma-Aldrich (Steinheim, Germany). Methyltrioxorhenium (MTO, 98%) and platinum catalyst on carbon (10 wt% Pt/C) were obtained from Alfa Aesar (Sulzbach, Germany). Hydrogen peroxide (aqueous, 30 wt%), potassium hydroxide pellets, formic acid (≥98.0%), and acetic acid (≥99.0%) were obtained from Merck (Darmstadt, Germany). Acetonitrile and tetrahydrofuran were from Acros organics (Geel, Belgium). Gold nanoparticle catalyst (1 wt% Au/TiO_2) from World Gold Council was obtained from Strem Chemicals (Kehl, Germany). *Tert*-butanol was from Lab-Scan (Gliwice, Poland). Pure oxygen for reaction was obtained from the gas supply facilities of the Faculty of Mathematics and Natural Sciences, University of Groningen. All materials were used as received without further purification.

4.2.2 Analytical Methods

Quantification of acid products was performed by high performance liquid chromatography (HPLC) using a calibration curve for each compounds (external standard method). The HPLC was equipped with a Hewlett Packard 1050 pump, a Biorad Aminex HPX-87H organic acid column and a Waters 410 refractive index detector. The mobile phase was an aqueous solution of sulphuric acid (5 mM) at flow rate of 0.55 mL/min. The column was operated at 60 ^{o}C.

Capillary electrophoresis (CE) was performed on a CE from Agilent Technologies, using a standard fuse capillary (75 μm i.d., 72 cm active length, and 80.5 cm total length) and a diode array detector (DAD). The CE was operated at a temperature of 20 ^{o}C and a voltage of -25 kV. Electropherograms were recorded at 350 nm with a reference at 200 nm. A buffer solution (pH = 4.6) from Agilent Technologies containing 5 mM cetyltrimethyl-ammonium bromide (CTAB) was used. The capillary was preconditioned prior to each measurement by flushing the buffer solution for 4 min at 1 bar.

GC-MS spectra for structural analysis were recorded on an HP 6890 model equipped with an HP1 5973 column (length 30 m, inside diameter 0.25 mm, film 0.25 μm) and with a mass selective detector. Peak identification was done using the NIST05a mass spectra library.

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ as the solvent at room temperature using a Varian AS400 NMR Spectrometer. For ^{1}H NMR spectra, a total of 32 scans was performed with a relaxation delay of 1 s while 4000 scans were recorded with a relaxation delay of 10 s for ^{13}C NMR spectra.

4.2.3 Experimental Methods

4.2.3.1 Catalyst-screening studies

Oxidation of LA using H_2SO_4-H_2O_2.

When performing this reaction, particular care should be taken since pure *gem* bis-hydroperoxide compounds are known to be shock, friction, temperature [46] and transition-metal sensitive [48].

Reaction in n-butanol: LA and H_2O_2 were mixed for 1 min. In a separate vessel, H_2SO_4 (662 μL) was dissolved in 20 mL n-butanol. A mixture of LA/H_2O_2 (1.16 gr LA, 10 mmol, 5.1 mL H_2O_2, 50 mmol) was added dropwise to a solution of H_2SO_4 (662 μL) in n-butanol (20 ml) with stirring for 10 minutes. After this period, the mixture was heated to 100 ^oC and allowed to react for 1 h. Subsequently, the reaction mixture was cooled to room temperature in a waterbath. Chloroform (100 mL) was added, and the organic phase was separated from the aqueous phase. K_2CO_3 (5 gr) was added and the suspension was stirred for 10 minutes, filtered, checked by peroxide test paper, and, when negative, the solvent was removed in a rotary evaporator. The sample was diluted with methyl *tert*-butyl ether, and analysed by GC-MS. Concentrations were determined by using calibration curves obtained by injecting n-butyl levulinate and di-n-butyl succinate at known concentrations.

Typical experiment in acetonitrile: In a reaction flask equipped with reflux condenser, a LA-H_2O_2 mixture (2.36 gr LA, 20 mmol, 10.2 mL H_2O_2, 100 mmol) was added under stirring at room temperature to a solution of H_2SO_4 (1324 μL, ~ 0.5 M) in acetonitrile (30 mL). After 10 min, the reaction mixture was heated to the desired temperature. This point was taken as time zero for the reaction. Samples were taken periodically to follow the reaction profile and analysed by HPLC and CE. The LA, SA, MA, AA, and FA concentrations were obtained using calibration curves for each component with at least five data points.

Oxidation of LA using Br_2-NEt_3-H_2O_2.

Typically, bromine (66 μL, 3.3 mmol) was added in three portions in a 15 min period to a solution of LA (1.18 g, 10 mmol) in acetonitrile (45 mL). Subsequently the mixture was heated to reflux for 1 h, then cooled to 50 ^oC. Triethylamine (2 mL, 14 mmol) was added and the reaction was allowed to continue for 1 h. ^1H NMR and HPLC indicated full conversion of the brominated LA during this period. Finally, hydrogen peroxide (5 mL, 50 mmol) was added either in 5 portions over a period of 25 minutes or directly to the reaction mixture. The mixture was heated to reflux and maintained at this condition for 1 h. Samples were taken after 30 min and 1 h. The samples were diluted with water and analysed by HPLC and CE.

Oxidation using $F_{14}CuPc$.

$F_{14}CuPc$ (71.8 mg, 0.08 mmol) and LA (1 gr, 8.3 mmol) were mixed together in acetonitrile (2 mL) and heated to 80 ^{o}C. At this temperature, hydrogen peroxide (0.8 mL, 8.3 mmol) was added dropwise within 1 min, and the mixture was maintained for 1 min at 80 ^{o}C, during which considerable amounts of gas phase components evolved. Subsequently a sample was taken, diluted in water, and analysed by HPLC and CE.

Oxidation using CuO.

CuO (0.25 g) and LA (5 g, 42.2 mmol) were added to acetonitrile (20 mL) in a reactor equipped with heating jacket, turbine-type stirrer, and a reflux condenser. The mixture was heated to 80 ^{o}C and subsequently hydrogen peroxide (22 mL) was added dropwise over a 5 min period and the mixture was maintained at this temperature for 1 h. Formation of gas bubbles was observed, indicative for hydrogen peroxide decomposition. During reaction, the mixture turned blue, an indication for the formation of soluble Cu species. After reaction, a sample was taken, diluted with water, filtered using a PTFE filter, and analysed by HPLC and CE. The remaining mixture was cooled to room temperature. The remaining solid was separated by centrifugation. Dichloromethane and water were added to allow phase separation of the organic and the aqueous phase. The aqueous phase was extracted several times with dichloromethane and the combined layers were dried using $MgSO_4$. The solvent was removed and the residue was analysed with GC-MS. For this purpose, 5 mg of the solid was placed in a 2 mL GC vial, then pyridine (100 μL) and BSTFA (100 μL) were added and the vial was capped. The vial was heated to 60 ^{o}C for 20 minutes and subsequently the sample was analysed using GC-MS.

Oxidation using $Na_2PtCl_4.4.5H_2O$.

The amount of water in the catalyst was determined by TGA analyses. $Na_2PtCl_4.4.5H_2O$ (93 mg, 0.2 mmol) and LA (273 mg, 2 mmol) were added to water or acetonitrile (835 μL) in a three-necked round bottom flask equipped with a condenser at room temperature. This mixture was heated to 85 ^{o}C. Hydrogen peroxide was added portion wise (2 drops) every 15 min for a total reaction time of 5h. After this time, sample was taken, diluted with water, filtered using a PTFE filter, and analysed by HPLC and CE.

4.2.3.2 Solvent-screening and optimisation studies using the H_2SO_4-H_2O_2 system

Reactions in water and diglyme were performed using a procedure as described above for acetonitrile. All experiments were carried out with a LA concentration of 0.48 M and a H_2SO_4 concentration of 0.5 M.

4.2.3.3 Oxidation reactions of biomass hydrolysates

Hydrolysis and dehydration of starch, cellulose, D-glucose and xylose were performed in a microwave batch reactor (40 mL) using 0.5 M H_2SO_4 in water (18 mL) at 165 °C for 1 h (glucose, cellulose, and starch) and 15 min for xylose, each using 2 gr of feedstock intake. After reactions, the humins were separated by centrifugation and a subsequent filtration using 0.2 μm PTFE filters. The filtrates were stored at -18 °C to avoid further hydrolysis. The hydrolysates were, when necessary, acidified with sulphuric acid to obtain a H_2SO_4 concentration of ~ 0.5 M. Ten folds molar excess of hydrogen peroxide (based on LA or furfural content in the hydrolysates) was added directly for these experiments. Oxidation reactions of the hydrolysates were performed at 105 °C for 4 h, except for hydrolysate from xylose, for 1 h.

4.2.3.4 Oxidation reaction of JCL seed shell hydrolysate

JCL seed shell was obtained by manual dehulling of JCL seeds. The shells were dried in an oven at 105 °C overnight, grounded, sieved using a 200 μm sieve and stored in a desiccator before use. Hydrolysis was performed in a microwave batch reactor (40 mL) using 1 M H_2SO_4 (18 mL) and 2 gr of the shell powder, at 165 °C, for 1 h. After reaction, the solids were separated by centrifugation and a subsequent filtration using 0.2 μm PTFE filter. The filtrate was stored at -18 °C to avoid further hydrolysis. The oxidation reaction was performed in a similar way as described above.

4.3 Definitions

Conversion of LA is defined as: $X_{LA} = \frac{C_{LA,i} - C_{LA,f}}{C_{LA,i}} \times 100\ \%$

where $C_{LA,i}$ and $C_{LA,f}$ is the initial and final concentration of LA (in molar), respectively.

Selectivity of SA is defined as: $S_{SA} = \frac{C_{SA}}{C_{LA,i} - C_{LA,f}} \times 100\ \%$

where C_{SA} is concentration of SA (in molar).

Yield of SA is defined as: $\eta_{SA} = X_{LA} \times S_{SA} = \frac{C_{SA}}{C_{LA,i}} \times 100\ \%$

4.4 Results and Discussion

4.4.1 Exploratory catalyst-screening studies

Several catalytic systems for the conversion of LA to SA using hydrogen peroxide and oxygen as oxidants were tested and the results are summarised in Table 1.

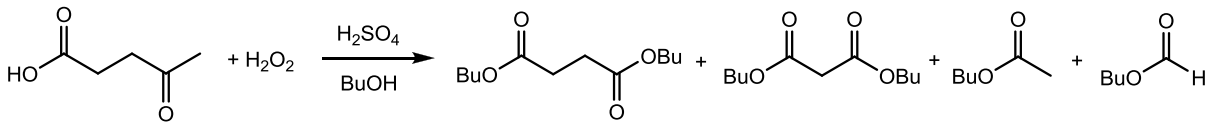
Table 1 Overview of catalyst-systems screened for the oxidative cleavage of LA to SA

Exp	Catalyst	Oxidant	Solvent	T [°C]	P_{abs} [bar]	X_{LA} [a)] [mol%]	S_{SA} [a)] [mol%]
1	H_2SO_4	H_2O_2	n-butanol	100	1	56[b)]	61[b)]
2	Br_2	H_2O_2	acetonitrile	80	1	43	9
3	$F_{14}CuPc$	H_2O_2	-	80	1	62	7
4	CuO	H_2O_2	acetonitrile	80	1	74	3
5	Na_2PtCl_4	H_2O_2	acetonitrile	85	1	51	6
6	CH_3ReO_3	H_2O_2	*t*BuOH or THF	rt	1	0[c)]	0[c)]
7	NaOH	H_2O_2	water	rt	1	0	0
8	$Mn_2L_2O_3.(PF_6)_2$	H_2O_2	acetonitrile	60	1	0	0
9	1% Au/TiO_2 or 10%Pt/C or $(PPh_3)_2PtO_2$	H_2O_2	KOH solution in water [1.8 M]	80	1	0	0
10	1% Au/TiO_2 or 10% Pt/C or $(PPh_3)_2PtO_2$	O_2	KOH solution in water [1.8 M]	80	6	0	0

[a)] calculated from HPLC analysis except when stated otherwise [b)] GC-MS (as dibutyl ester of SA); [c)] ^{1}H NMR

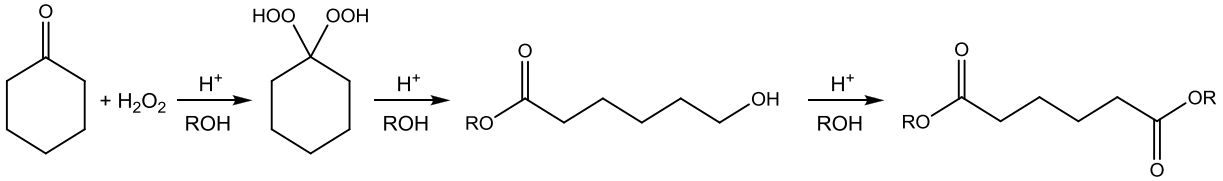
Five of the catalyst systems proved to be active for the oxidation reaction with LA conversions between 43 and 74 mol% and a SA selectivity ranging between 3 and 61% and these will be discussed in more detail in the following.

The use of the system H_2SO_4-H_2O_2 in n-butanol (entry 1) was based on the work of Terent'ev [47], on the oxidative cleavage of cyclohexanone to dibutyl-esters of adipic acid in n-butanol as solvent. To the best of our knowledge, this system has never been used for open chain ketones such as in LA. A reaction at 100 °C in n-butanol (LA concentration of 0.37 M, 1 h) resulted in 56 mol% LA conversion (GC-MS). The remaining LA was present as the n-butyl ester, indicative for an *insitu* esterification at these conditions. The main product was the di-n-butyl ester of SA (61 mol% selectivity, GC-MS), other byproducts were di-n-butyl esters of malonic acid (MA) and mono-n-butyl esters of acetic acid (AA) and formic acid (FA, see eq. 4).



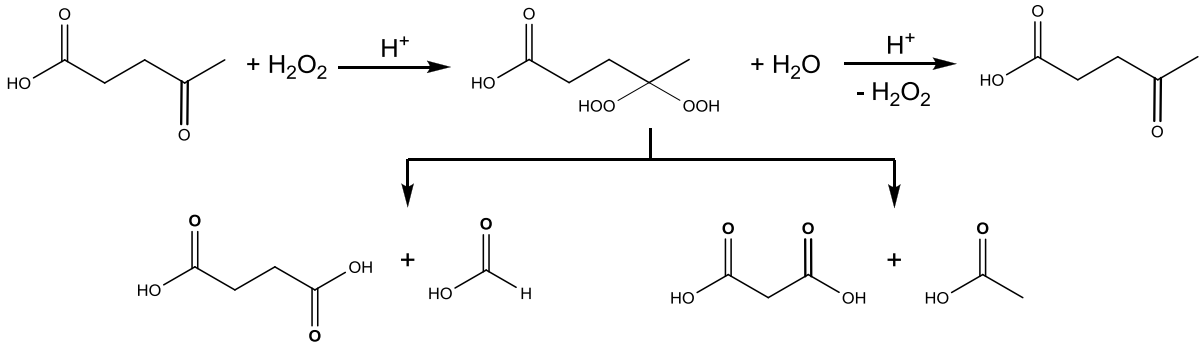
(eq. 4)

In addition, the n-butyl ester of butanoic acid was also detected as a side product, an indication for the oxidative esterification of n-butanol. The reaction is likely similar to the oxidation of cyclohexanone to di-ester of adipic acid, which involves the initial formation of *gem* bis-hydroperoxides followed by the oxidative cleavage to a hydroxyl-acid and subsequently to the di-acids (Scheme 2) [46].



Scheme 2 Oxidative cleavage of cyclohexanone to the di-ester of adipic acid [46]

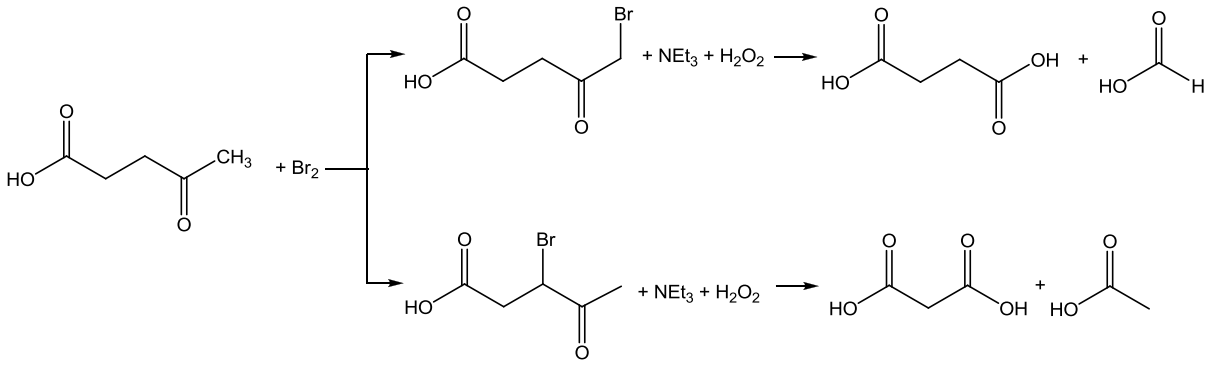
Reactions of the intermediate bis-hydroperoxide may either lead to SA and FA (cleavage of C4-C5), or MA and AA (cleavage of C3-C4, Scheme 3). A possible non-productive side reaction is the reaction of the intermediate *gem* bis-hydroperoxide with water to the starting material [49].



Scheme 3 Oxidative cleavage of LA to (di-)carboxylic acids via *gem* bis-hydroperoxides

The second synthetic methodology explored in this study involves a catalytic oxidative cleavage using I_2-H_2O_2-NEt_3 [50]. This system is known to be effective for the oxidative cleavage of 1,3-dicarbonyl compounds with carboxylic acids yield up to 95% when using H_2O_2 as the oxidant. However, to the best of our knowledge, this method has never been used for the oxidative cleavage of open chain mono-ketones. Exploratory experiments were performed using iodine or hydrogen iodide in combination with triethylamine and hydrogen peroxide at 80 °C in acetonitrile. However, LA did not react at these conditions (HPLC, CE). When using Br_2 instead

of I_2, LA was reactive, leading to a SA selectivity of 9 mol% at a LA conversion of 43 mol% (mol ratio bromine to LA of 1). Reactions with a higher bromine to LA ratio (2:1 and 4:1) led to higher LA conversions of 56 and 83 mol%, respectively. However, the SA yields were about similar as for the reaction at a ratio of 1 (7 and 5 mol%, respectively). A possible explanation for this low selectivity is the low selectivity of the bromination of LA, the proposed first step in the reaction mechanism (Scheme 4). For instance, MacDonald [51] reported that the bromination of LA in methanol led to almost exclusively to 3-bromo-LA. A well-known method to obtain the desired reverse chemo-selectivity is to perform the bromination in the presence of urea [52]. This approach was also tested, but proved not successful and the conversion of LA was negligible.



Scheme 4 Proposed pathway for the bromination and subsequent oxidative cleavage of LA to SA, FA, AA, and MA

Catalytic oxidation systems based on Cu [53] and Pt [54] were also explored. For initial test with Cu, a commercially available copper tetradecafluoro phthalocyanine complex was used as the catalyst in combination with H_2O_2 (entry 3). The reaction was performed at 80 °C in neat LA for short reaction times (1 min), leading to a LA conversion of 62 mol%. HPLC and CE analysis revealed the presence of SA in the reaction mixture, though selectivity to SA was low (7 mol%). Major products were AA and FA. Follow-up experiments were performed using a heterogeneous copper (II) oxide catalyst (entry 4) in acetonitrile at 80 °C for 60 min. High LA conversion of up to 74% were observed, though SA and MA were found in small quantities only. Major products were FA, AA and 3-hydroxy propionic acid (GC-MS). The results using a Pt catalyst instead of Cu (Na_2PtCl_4, entry 5) were also not encouraging with respect to SA and the maximum SA selectivity was 6 mol% at 51 mol% LA conversion.

Other oxidation methods involving $MeReO_3$ [43] (entry 6), NaOH [44] (entry 7), a homogeneous Mn catalyst [55] (entry 8, catalyst was prepared by according to a reported procedure [56]), all with H_2O_2 as the oxidant and Au/TiO_2, Pt/C and $(PPh_3)_2PtO_2$ [30] in combination with either H_2O_2 (entry 9) or oxygen (entry 10) showed no LA conversion under the prevailing reaction conditions and as such were not successful.

To conclude, sulphuric acid in combination with H_2O_2 was the best oxidation system for the conversion of LA to SA. Accordingly, this system was used for further optimisation studies.

4.4.2 Solvent screening

Initial screening studies for the H_2O_2-H_2SO_4 system were performed in n-butanol and resulted in the formation of the di-n-butyl esters of SA (*vide supra*). To obtain SA in the acidic form, subsequent reactions were carried out in three polar solvents (acetonitrile, water, and diethylene glycol dimethyl ether (diglyme)). For comparison, all reactions were carried out at 80 °C, 0.5 M H_2SO_4, $C_{LA,i}$ = 0.48 M, and a molar excess of H_2O_2 to LA of 5:1. All reactions were conducted at least in duplicate and the LA conversion and SA selectivity after 4 h are within 3 mol% abs.

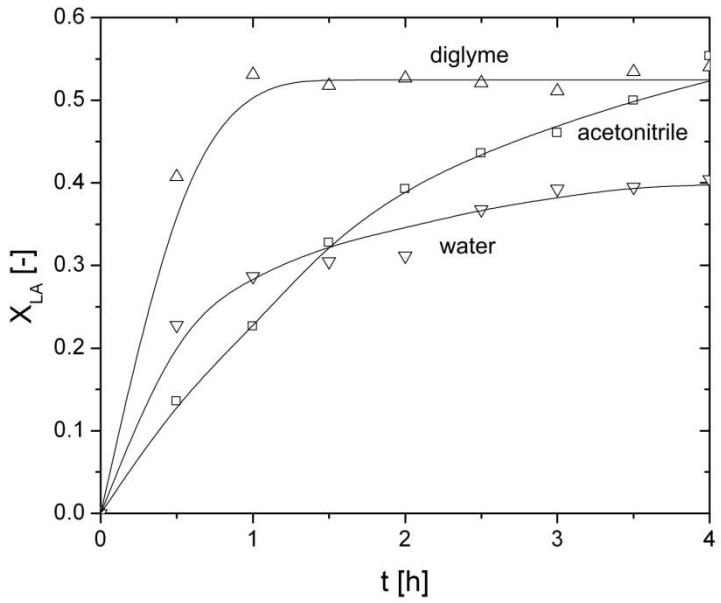
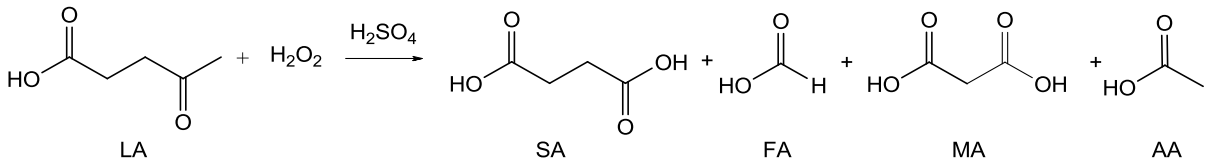


Fig. 1 Conversion of LA versus time for reactions in different solvents (trendlines for illustrative purpose only). Reaction conditions: $C_{LA,i}$= 0.48M, T = 80 °C, ~ 0.5M H_2SO_4, molar excess H_2O_2:LA = 5:1 (direct addition).

The conversion of LA in acetonitrile as well as other solvents versus time is given in Fig. 1. Full conversion was not achieved in 4 h. The main products are SA, FA, MA, and AA (eq. 5). SA was formed in 72 mol% selectivity at 54 mol% LA conversion after 4 h reaction time, giving a yield of 39 mol% (Fig. 2).



(eq. 5)

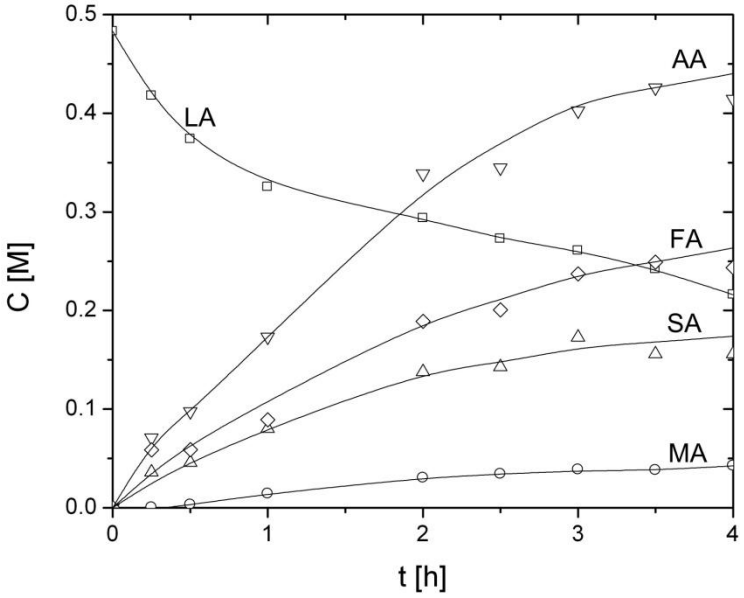


Fig. 2 Typical reaction profile in acetonitrile (trendlines for illustrative purpose only). Reaction conditions: $C_{LA,i}$= 0.48M, T = 80 °C, ~ 0.5M H_2SO_4, molar excess H_2O_2:LA = 5:1 (direct addition).

Based on the mechanistic proposal in Scheme 3, SA and FA as well as MA and AA are expected to be formed in equimolar amounts. However, the SA concentrations are significantly lower than those of FA during the run, indicative for another pathway leading to FA. When considering the carbon balance and assuming that SA is stable under reaction conditions (*vide infra*) and not involved in subsequent reactions, a MA concentration of about 0.07 M is expected after 4 h. Stoichiometric considerations predict a similar AA concentration. This is not the case, see Fig. 2, and the concentration of MA is about half of this value and the AA concentration is 5 times higher. Likely, AA is formed by a second reaction pathway, independent from the one that starting from LA.

To get more insights in AA formation, reactions in acetonitrile under typical reaction conditions were performed in the absence of reagents and with SA or MA as the reactants. The oxidation of SA using the H_2O_2-H_2SO_4 catalytic system at 80 °C for 4 h did not result in appreciable SA conversion. Thus, at the timescale of our experiments, SA is stable. A similar reaction with MA resulted in about 30 mol% MA conversion, indicating that MA is prone to subsequent oxidation reactions (Fig. 3).

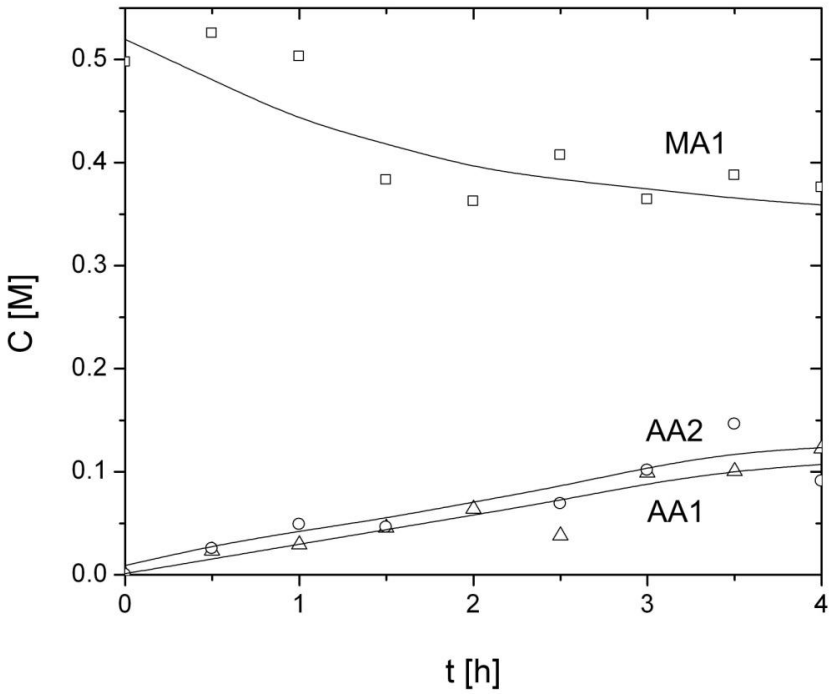
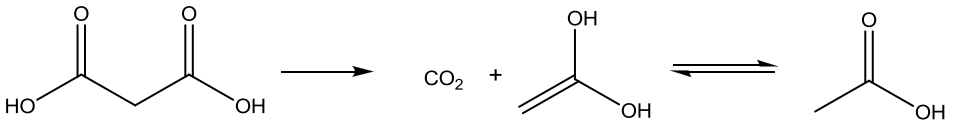


Fig. 3 Concentration versus time profile for oxidation reaction of MA and a blank reaction without substrates (trendlines for illustrative purpose only). MA1 and AA1: MA and AA profile for reaction with MA as substrate, AA2: AA profile for blank reaction

The main product when using MA as the substrate was AA, possibly by a decarboxylation reaction (eq. 6) [57].

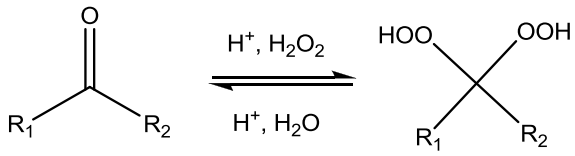


(eq. 6)

However, an alternative explanation for AA formation was evident when performing a reaction in the absence of substrates at 80 ^{o}C (blank reaction). The main product in this case was AA, formed in a concentration of about 0.1 M at the end of the 4 h run. Thus, it appears that acetonitrile is also reactive under these conditions and contributes to the formation of AA. In this respect, it is well possible that the active oxidation species in acetonitrile is a peroxycarboximidate (a Payne type of reagent from acetonitrile). Typically, it is formed *insitu* by a base catalysed perhydrolyses of acetonitrile [58,59], though may also occur at a certain extent in acidic conditions. After reaction, the resulting acetamide (CH_3CONH_2) may hydrolyse to AA [60].

Alternative polar solvents (water and diglyme) were explored for the oxidation reaction. Conditions were similar as for the oxidations in acetonitrile ($C_{LA,i}$ 0.48 M, 5

folds excess of H_2O_2, 80 °C, 4 h). When performing the reaction in water, the LA conversion was 38 mol% after 4 h (Fig. 1), c.f. 54 mol% in acetonitrile. The initial rate in water is higher than in acetonitrile, however, it levels off more rapidly and ultimately gives a lower conversion than in water. A possible explanation is the occurrence of hydrolysis of the intermediate *gem* bis-hydroperoxide to the starting materials (eq. 7). Nikishin *et. al.* [49] proved the occurrence of such reactions by hydrolysing cyclic and aliphatic *gem* bis-hydroperoxide compounds using H_2SO_4 as catalyst in THF solvent at room temperature. This equilibrium reaction likely will have a negative effect on the overall reaction rate of LA to SA in water when it is relatively slow on the timescale of the subsequent reactions.



(eq. 7)

The concentration profile of SA versus time in water is given in Fig. 4. The SA concentration after a 4 h run was 0.08 M, corresponding with a yield of 16 mol% (at 38 mol% LA conversion). This value is considerably lower than for acetonitrile (39 mol% yield after 4 h), mainly due to a lower selectivity to SA.

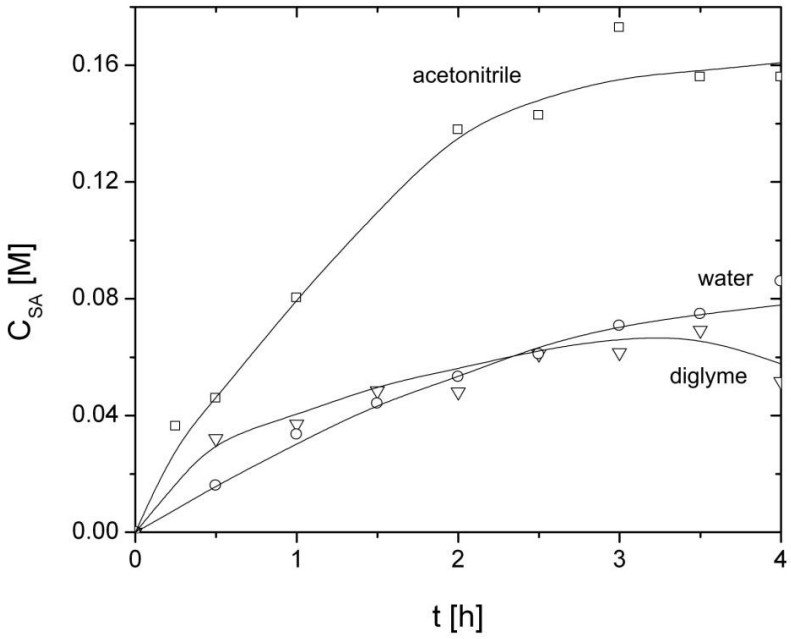


Fig. 4 Concentration profile of SA during reaction in different solvents (trendlines for illustrative purpose only). Reaction conditions: temp : 80 °C, ~ 0.5M H_2SO_4, molar excess H_2O_2:LA = 5:1 (direct addition).

Of all solvents tested, the highest initial reaction rates were obtained in diglyme, see Fig. 1 for details. However, the reaction rates level off rapidly and after about 1-1.5 h, the concentration of LA remained constant. The calculated yield of SA after 4 h is 13 mol%, which is lower than for acetonitrile (39 mol%) and water (16 mol%). Main products are FA and AA, an indication for considerable over-oxidation when using diglyme as the solvent. Ethers such as diglyme are known to be easily oxidised at 80 °C to form peroxides [29], which may enhance over-oxidation reactions.

4.4.3 Optimisation experiments

Process conditions like temperature and H_2O_2 addition protocol (direct addition or dropwise) were varied for reactions in acetonitrile and water to optimise the SA yield. All reactions were performed at least in duplicate and the average values with standard deviations are given. The initial concentration of LA (0.48 M) and H_2SO_4 concentration (0.5 M) were constant. The LA conversion, SA selectivity and SA yield were determined after 4 h batch time and the results are presented in Table 2.

Table 2 Effect of process conditions on LA conversion and SA selectivity in acetonitrile and water

Entry	Solvent	H_2O_2:LA molar ratio (addition method)	T [°C]	X_{LA} [a] [mol%]	S_{SA} [a] [mol%]	η_{SA} [a] [mol%]
1	Acetonitrile	5:1 (direct)	70 ± 2	51 ± 2	43 ± 2	22
2	Acetonitrile	5:1 (direct)	80 ± 2	54 ± 2	72 ± 3	39
3	Acetonitrile	5:1 (direct)	≈ 90[b]	80 ± 1	64 ± 3	51
4	Acetonitrile	10:1 (direct)	80 ± 2	60 ± 2	47 ± 2	28
5	Acetonitrile	5:1 (dropwise in 1h)	80 ± 2	55 ± 2	73 ± 1	40
6	Water	5:1 (direct)	80 ± 2	38 ± 1	42 ± 2	16
7	Water	5:1 (dropwise in 1h)	≈105[b]	72 ± 1	21 ± 1	15
8	Water	10:1 (dropwise in 1h)	≈105[b]	85 ± 1	13 ± 2	11
9	Water	12.5:1 (dropwise in 1h)	≈105[b]	85 ± 1	15 ± 1	13

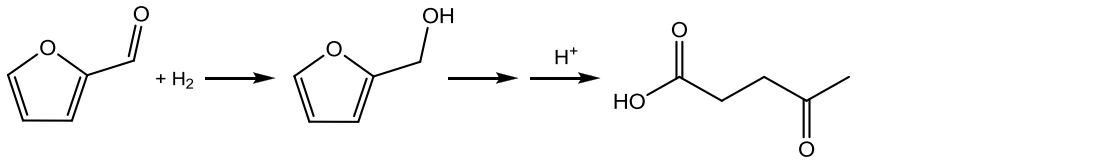
[a]Average of at least two experiments [b]Reflux conditions

Temperature has a major effect on the yield of SA. Highest SA yields (51%) in acetonitrile were obtained at a temperature 90 °C (entry 3, Table 1), which is a considerable improvement compared to the value of 39% in the screening study at 80°C. The effect of the H_2O_2 addition protocol was limited, both conversion and selectivity were similar when adding the H_2O_2 at once or dropwise in 1 h (c.f. entry 2 and 5). The use of a larger excess of H_2O_2 to LA (10:1 instead of 5:1, entry 4) resulted in a slightly higher LA conversion, though a considerably reduced selectivity to SA and as such was not successful.

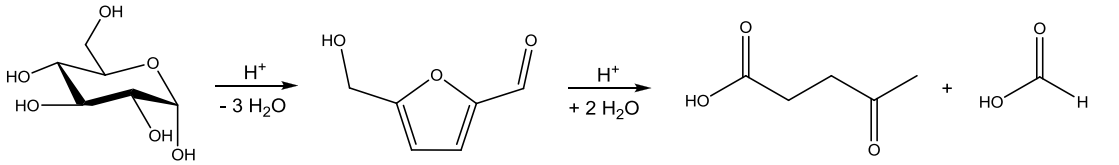
In water, a strong effect of the temperature on the LA conversion was observed (60% at 80 °C versus 85% at 105°C, entry 6 and 8). However, the selectivity to SA reduces dramatically at higher temperatures (42% to 21%). Further experiments using different molar ratios between hydrogen peroxide and sulphuric acid also did not lead to significant SA yield improvements. Thus, highest SA yields were obtained in acetonitrile as the solvent.

4.4.4 Succinic acid from furfural

Two technologies have been proposed for the production of LA, i) the reduction of furfural to furfuryl alcohol followed by an acid catalysed rearrangement to LA (eq. 8) [61] and ii) the acid catalysed dehydration of C6 sugars in lignocellulosic biomass (eq. 9) [62].



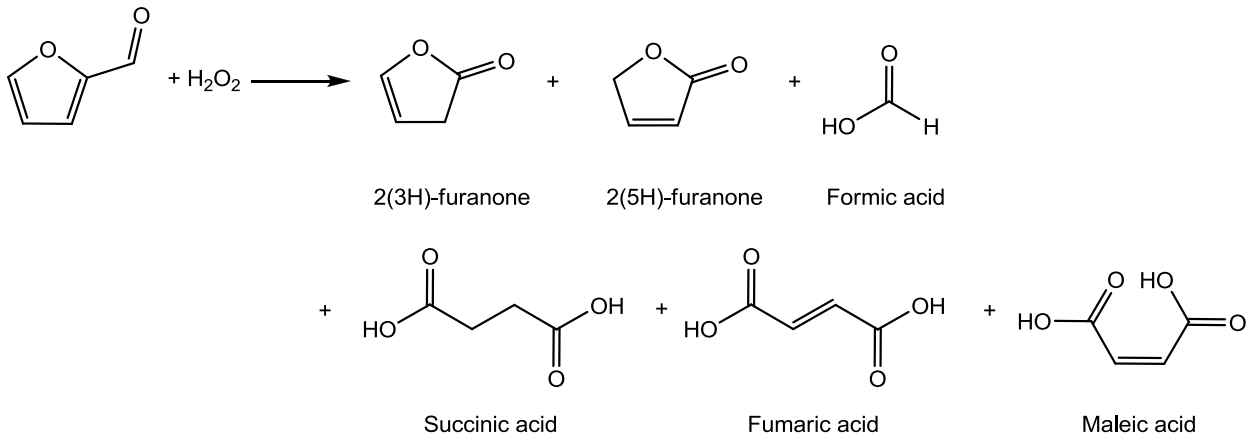
(eq. 8)



(eq. 9)

Route 1 is commercially operated in China, route 2 is under development by a.o. BioFine (*vide supra*). Route 2 also results in the formation of furfural due to hydrolysis of the C5 sugars in the biomass source. Thus, there is a clear incentive to see whether furfural is also suitable as a starting material for SA synthesis. For route 1, the direct use of furfural instead of LA for SA synthesis leads to a considerable reduction in the number of conversions steps whereas route 2 allows for conversion of not only the C6 sugars but also the C5 sugars to SA, thereby offering the potential to obtain higher SA yields.

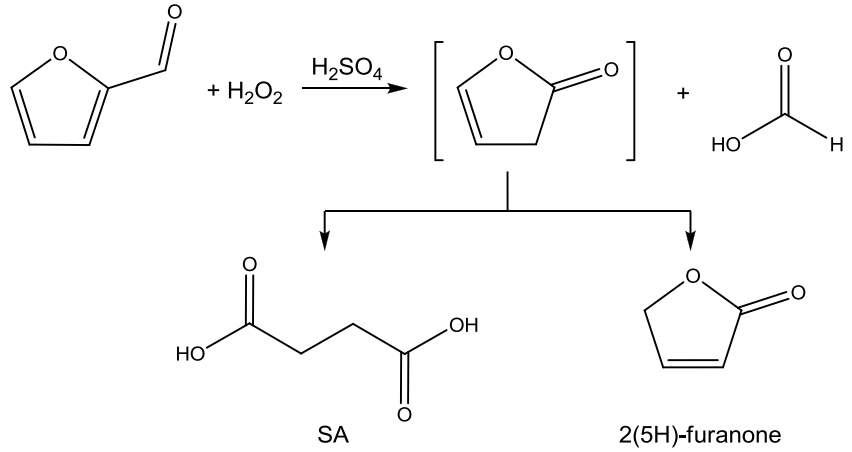
Scattered literature data is available on the oxidation of furfural to SA. Oxidation of furfural with Caro's acid was reported back in the 1900's to give SA and FA [63,64]. A number of papers report the oxidation of furfural using H_2O_2 both in the presence or absence of metal catalysts [65-70]. Furfural was oxidised using a 50% solution of H_2O_2 in water at room temperature without any added catalyst to give a mixture of hydroperoxide compounds as intermediates, and 2(3H)-furanone, 2(5H)-furanone, formic acid, and di-acids (SA, fumaric, maleic) as final products (Scheme 5). SA was obtained in 20-50 wt% yield. A catalytic reaction with $VOSO_4$ (sodium acetate buffer, 60 °C, 12% H_2O_2 solution) [68] resulted in the formation of SA (max 35 wt% yield), β-formylpropionic acid, and 2(5H)-furanone. Considerably lower SA yields (< 20 wt%) were obtained using other catalysts (Na_2MoO_4, $NaHSeO_3$ [69], Nb_2O_5, and $Nb(OAc)_2$ [70].



Scheme 5 Product distribution from un-catalysed oxidation of furfural with hydrogen peroxide

Recently, the oxidation of furfural to near quantitative (90 wt%) SA yields using a two-step procedure was reported. It involves the oxidation of furfural by hydrogen peroxide in water under reflux conditions to SA and 4-oxobutanoic acid [71]. In a subsequent step at higher pH, the 4-oxobutanoic acid is also oxidised to SA.

A number of preliminary experiments were performed on the oxidation of furfural to SA using the H_2O_2-H_2SO_4 oxidation system in both water and acetonitrile. In acetonitrile (80 ^oC), furfural was converted completely within 30 minutes, giving SA in about 20 mol% yield. 2(5H)-furanone was formed in equimolar amount with SA (HPLC), together with formic acid. A possible reaction pathway involves the initial formation of 2(3H)-furanone and formic acid [65,66,72-74], after which the former reacts to SA and 2(5H)-furanone (Scheme 6).



Scheme 6 Oxidation of furfural with hydrogen peroxide to SA, 2(5H)-furanone, and formic acid

The oxidation of furfural was also performed in water (reflux, about 105 °C) using a ten-folds molar excess of H_2O_2. Furfural was fully converted within 10 minutes reaction time. Main reaction products were SA, 2(5H)-furanone and formic acid (not quantified). The maximum SA yield was 40 mol%. Extended reaction time resulted in the decomposition of both SA and 2(5H)-furanone to unknown products (Fig. 5).

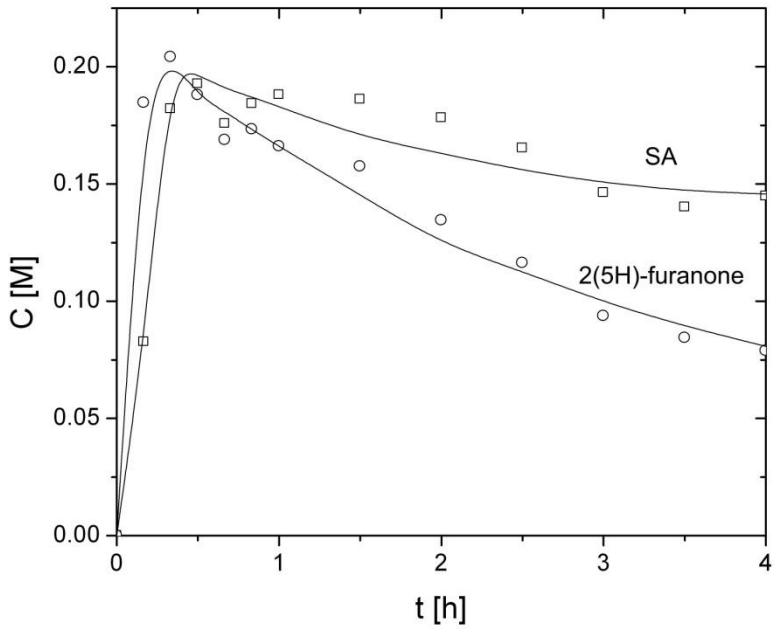


Fig. 5 Concentration profile of SA and 2(5H)-furanone from furfural in water (trendlines for illustrative purpose only). Reaction conditions: initial concentration of furfural = 0.46 M, 10 fold molar excess of H_2O_2, H_2SO_4: ~ 0.5 M, T = 105 °C.

To conclude, our results indicate that the oxidation of furfural using the H_2O_2-H_2SO_4 system is better performed in water than in acetonitrile. Complete furfural conversion was obtained in both solvents, though the SA yield in water (40 mol%) was considerably higher than in acetonitrile (20 mol%).

4.4.5 Succinic acid from carbohydrate sources

Exploratory studies were performed on a two-step approach to obtain SA from abundantly available biopolymers (starch, cellulose), their hydrolysed monomers (D-glucose and xylose) and a lignocellulosic biomass source in the form of *Jatropha curcas* L. (JCL) seed shells. The latter is a waste product from the Jatropha biodiesel industry and contains about 44% of polysaccharides, the remainder being lignin (44%), extractives and ash [75]. The two step approach involves i) the acid catalysed dehydration of the feed in water to LA and/or furfural and the ii) subsequent oxidation of the hydrolysate by hydrogen peroxide to SA. The advantage of this

approach is that work-up of LA is not required and the catalysts used for the first hydrolysis step is also applied in the subsequent oxidation step to SA. The initial hydrolysis reaction was carried out at 165 °C for 60 min, except for xylose where 15 min reaction time was applied. Experiments were conducted in a microwave device using 0.5 M H_2SO_4 solutions in water, the only exception being JCL seed shell, which was hydrolysed using 1M H_2SO_4. After hydrolysis, the insolubles (humins) were separated by centrifugation of the hydrolysates. Analysis of LA/furfural concentration in the hydrolysates was performed by HPLC. An overview of the results is provided in Table 3.

Table 3 Acid catalysed hydrolysis of various substrates to LA/ furfural and subsequent oxidation to SA

Feedstock	T [°C]	Hydrolysis time [min]	LA yield [mol%][a]	Furfural yield [mol%][a]	Oxidation time [h]	SA yield[e] [mol%]
Glucose[b]	165	60	44	-	4	23 (10)
Xylose[b]	165	15	-	31	1	23 (7)
Cellulose[c]	165	60	37	-	4	22 (8)
Corn starch[c]	165	60	40	-	4	16 (6)
JCL seed shell[c,d]	165	60	25	-	4	25 (6)

Reaction conditions: 0.5 M H_2SO_4, for oxidation: 10 folds of H_2O_2 for oxidation, ≈105 °C, [a]for glucose and xylose, yield = mol LA (or furfural)/mol feedstock x 100%; for starch, cellulose, and JCL seed shell, yield = mol LA/mol C6 sugar unit in feedstock x 100%; [b][reactant] = 1 M, [c] 10 wt% solids, [d]hydrolysis was carried out using 1 M H_2SO_4; [e]for glucose and xylose, yield = mol SA/(mol feedstock) x 100%; for starch, cellulose, and JCL seed shell, yield = mol SA/mol LA (or furfural) in hydrolysate x 100%; in brackets: yield = mol SA/(mol C6 or C5 sugar unit in feedstock) x 100%

The amounts of LA and furfural (in case of xylose) in the hydrolysates are in agreement with literature data [76,77]. Oxidation of the hydrolysates resulted in SA yields between 16 to 25 mol% based on the LA or furfural content in the hydrolysates, which corresponds to 6 up to 10 mol% SA yield based on the C6 sugar content in the feedstock. Thus, the synthesis of SA from various C5 and C6-sugars as well as biopolymers (starch, cellulose) using a two step hydrolysis/oxidation approach with sulphuric acid has been demonstrated, though further research activities will be required to increase the SA yields.

4.5 Conclusions

Exploratory catalyst screening studies have been performed on the oxidation of LA to SA at mild conditions. Best results were obtained using sulphuric acid in combination with hydrogen peroxide, giving a SA yield of 40 mol% (73 mol% selectivity at 55 mol% LA conversion). The synthetic methodology was also applied for furfural, leading to a SA yield of 40 mol%. As such, the H_2SO_4-H_2O_2 system has potential for the conversion of furfural and LA rich aqueous streams, obtainable by the acid catalysed conversion of lignocellulosic biomass at elevated temperatures (180-220 °C) to SA and this was demonstrated experimentally using a waste stream of the JCL oil seed pressing industry. Further optimisation studies and techno-economic evaluations will be required to assess whether the methodology developed here is a feasible alternative for the current commercial fermentation route to SA.

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Chapter 5

Chemical modifications of *Sterculia foetida* L. oil to branched ester derivatives

Summary

An experimental study to modify *Sterculia foetida* L. oil (STO) or the corresponding methyl esters (STO FAME) to branched ester derivatives is reported. The transformations involve conversion of the cyclopropene rings in the fatty acid chains of STO through various catalytic as well as stoichiometric reactions. Full conversion of the cyclopropene rings was obtained using Diels-Alder chemistry involving cyclopentadiene in water at 40 ^{o}C without the need for a catalyst. Olefin metathesis reactions were performed using a Grubbs 2nd generation catalyst and cyclopropene ring conversion was ≥ 99 and 54 mol% with 2,3-dimethyl-2-butene and 1-octene, respectively. Oxidation reactions were performed using established epoxidation (Sharpless) and dihydroxylation (Prilezhaev) protocols using aqueous hydrogen peroxide as the oxidant. For both reactions, full conversion of the cyclopropene rings was obtained at RT to yield the corresponding α,β-unsaturated ketone in good selectivities. Rearrangement reactions of the cyclopropene rings to the corresponding conjugated diene were successfully performed using homogeneous and heterogeneous palladium catalysts. Excellent conversions (≥ 99%) were obtained using homogeneous palladium catalyst in a biphasic cyclohexane-water mixture (1:1) at 90 ^{o}C. Relevant cold flow properties of all products were determined and compared to crude STO and STO FAME. Best results were obtained for the metathesis products of STO with 1-octene, with a cloud point (CP) and pour point (PP) of -12 ^{o}C.

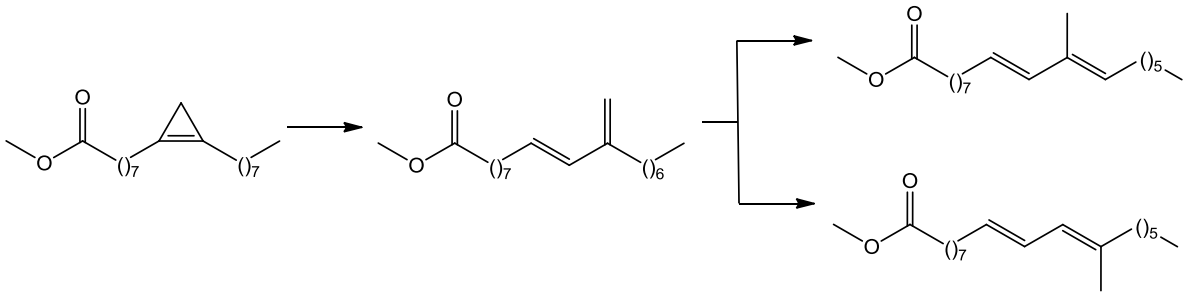
Keywords: Branched ester derivatives, chemical modifications, *Sterculia foetida* L. oil

5.1 Introduction

Sterculia foetida L., belonging to the family of Sterculiaceae and the order of Malvales, is a tropical tree with oil bearing seeds. The tree is natively wide spread from east Africa to north Australia and also grows in Indonesia [1]. The shape and size of the kernels resemble that of olives and as such the tree is also known as "Java olive". Other trivial names include wild almond tree, hazel sterculia, and poon [1,2]. In middle Java, the productivity of *Sterculia foetida* L. is reported to range between 450 - 2080 kg dry seeds/tree/year. When assuming a plant population of 66 trees/ha in a plantation wise setting, the seed yield ranges between 30 – 137 tons dry seeds/ha/year. Typically, 60% of the seed consist of seed kernel and the oil content of the seed kernel may be as high as 50 - 60 wt% (dry basis). The latter values are comparable to other tropical oil seeds such as Jatropha and rubber (60 wt%) as well as castor and Karanja (50 wt%) [2]. With these data, an oil productivity between 10 – 50 tonnes oil/ha/year may be estimated. This is high compared to that of *Jatropha curcas* L. (up to 2 tons oil/ha/year) or palm (currently at 3 - 6 tons oil/ha/year) [3]. However, this is only a very rough theoretical estimate as to the best of our knowledge Sterculia plantations do not exist to date and yield data need to be verified using scientifically sound methods.

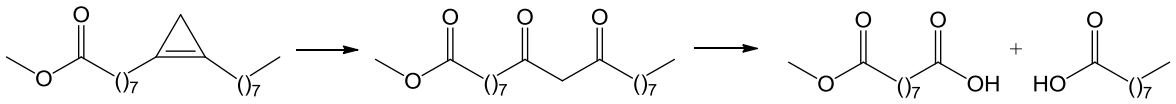
The oil from the *Sterculia foetida* L. (STO) seeds is considered non-edible, though a recent study indicates that the oil has potential as a health supplement to reduce belly fat built up [4]. STO contains fatty acids with cyclopropene units (CPEFA), which may account up to 70 wt%, in the form of sterculic acid (9,10-methylene-9-octadecenoic acid) and malvalic acid (8,9-methylene-8-heptadecenoic acid) [5]. This amount is the highest among all other plant oils containing cyclopropene rings [6]. In plants, sterculic acid is formed from oleic acid [7,8]. Malvalic acid is derived from sterculic acid by α-oxidation at the carboxylic end to the intermediate (R)-2-hydroxysterculic acid followed by cleavage to malvalic acid [9,10]. Both fatty acids are found in the roots, leaves, stems, and callus tissues in plants belonging to the Malvaceae family [11,12], and are mentioned to have anti-fungal activity [13]. Sterculic acid may also be obtained by chemical synthesis by the addition of a methylene unit to stearolic acid (9-octadecynoic acid, C18:3) [14].

The cyclopropene unit is very reactive due to a high strain energy (approximately 50 kcal/mol) [15]. The presence of this reactive functional group renders STO a very interesting feedstock for the production of oleochemicals. Rearrangement and subsequent hydrogenation reactions of STO methyl ester using heterogeneous palladium and rhodium on carbon catalysts to obtain methyl branched derivatives have been reported by Pryde [16,17]. The rearrangement reaction was performed under N_2 at 150 ^{o}C for 9 h, followed by a hydrogenation reaction at room temperature at 40 psi H_2 pressure for 1h. Rearrangement reactions of the cyclopropene rings in STO methyl esters were also reported to be catalysed by SiO_2 under N_2 at 160 ^{o}C for 15 min [18]. Both rearrangement systems led to the formation of isomeric fatty acid methyl esters containing methylene- and methyl-branched isomers in conjugation with a C-C double bond in the fatty acid chain (eq. 1).



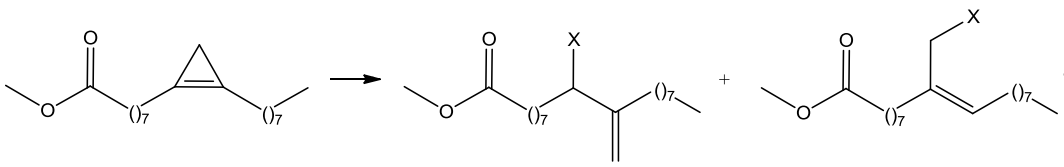
(eq. 1)

Gellerman [18] reported the hydrogenation of the cyclopropene rings in STO methyl esters to the corresponding cyclopropane rings using Pd-Pb on $CaCO_3$ as catalyst in methyl acetate as solvent at atmospheric pressure for 5 min. Oxidation of sterculic acid using potassium permanganate was reported to give an α-ketol, which was characterised as 9,11-dioxo-nonadecanoic acid, after a more detailed study using a range of analytical methods by other groups [19] (eq. 2). This compound was also formed by oxidation using ozone in anhydrous ethyl acetate at -25 °C for 30 minutes followed by hydrogenation using Pd/C in combination with hydrogen gas (5 h at 0 °C) [20]. Oxidation of 9,11-dioxo-nonadecanoic acid by hydrogen peroxide in acetic acid under reflux conditions for 1 h gave 1,9-nonanedioic acid and nonanoic acid as the only fission products [20].



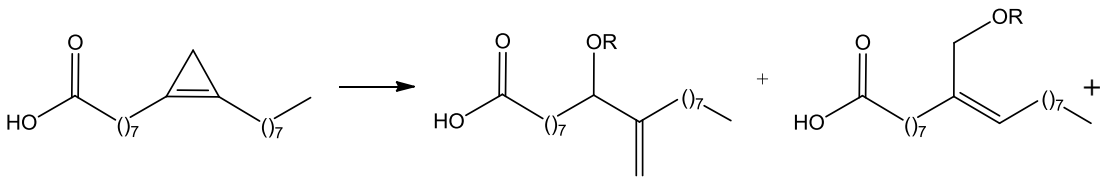
(eq. 2)

Reduction of sterculic acid with lithium hydride in ether gave sterculyl alcohol. Subsequent hydrogenation reactions of this alcohol using Pd and Pt catalysts revealed that the cyclopropene ring was kept intact during reduction [20]. Halogenation reactions of CPEFA with concentrated aqueous hydrogen halides in acetic acid for 1 h gave isomeric mono-unsaturated monohalo compounds [21] (eq. 3).



+ isomers (eq. 3)

Polymerisation of sterculic acid was reported by inter-molecular addition of the carboxylic acid group to the cyclopropene unit of another fatty acid chain [22,23] (eq 4, where R is a sterculic acid chain).



+ isomers (eq. 4)

Branched ester derivatives of vegetable oils have interesting product properties. Ester derivatives with long, aliphatic branches on the fatty acid chains show improved flow-ability properties at low temperatures compared to the pure plant oils as the branches inhibit crystallisation [24]. Ester derivatives with unsaturated cyclic structures in the fatty acid chain, for example those resembling norbornene-like structures, may find applications as reactive building blocks in resins and/or packaging material [25, 26], as well as reactive monomers in coatings and paints [27,28]. Ester derivatives with conjugated dienes in the fatty acid chains are of interest as reactive compounds in coating formulations [29]. Furthermore, a recent study showed that fatty acid derivatives containing α,β-unsaturated ketone units in the fatty acid chains may serve as reactive precursors for thermoset polymers [30].

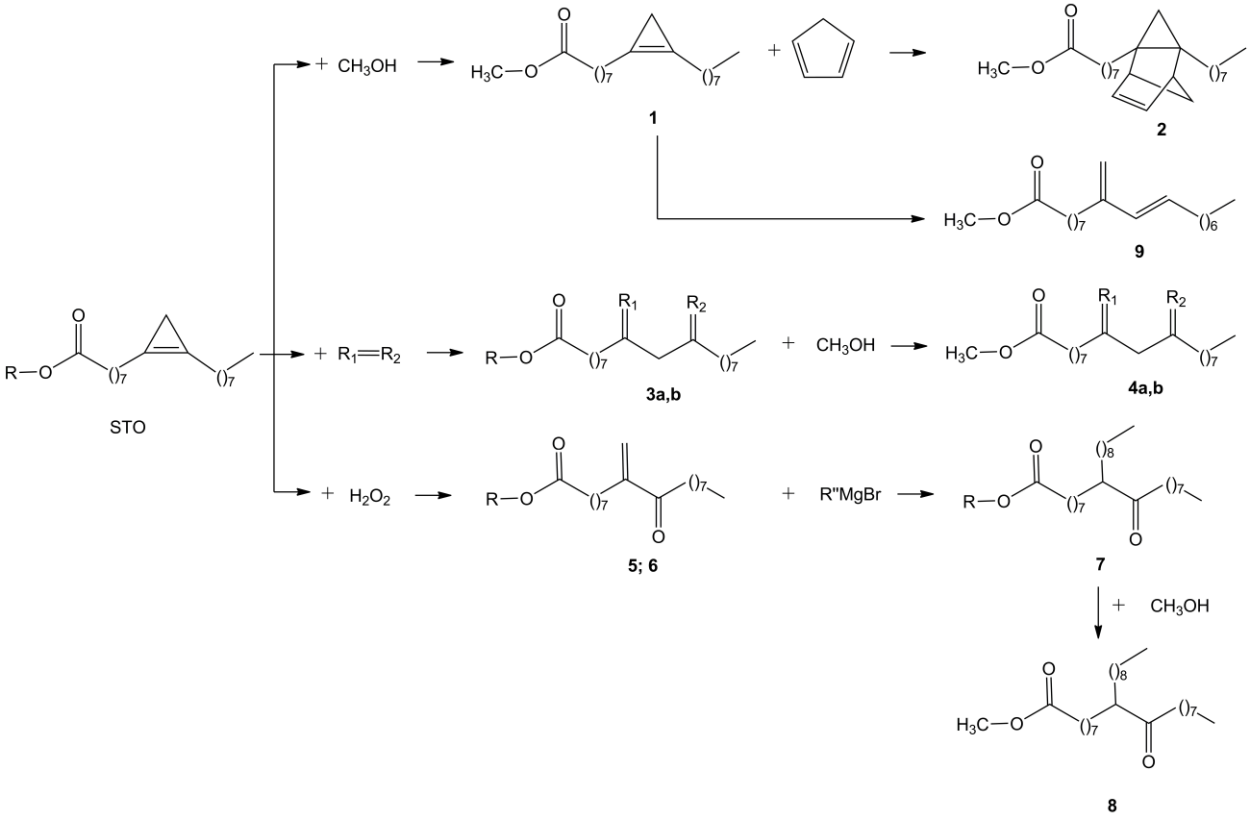


Fig. 1 Chemical modifications of STO to branched ester derivatives. (R= remaining triglyceride structure, R1,R2= substituents of the olefin, R"= n-octyl)

We here report an experimental study to introduce branches in the fatty acid chains by modification of the cyclopropene rings of STO using both catalytic and stoichiometric chemistry. These include Diels-Alder, olefin metathesis, oxidation, and rearrangement reactions (Fig. 1). The relevant cold flow properties of the products were determined and compared to STO and STO FAME. In addition, the storage stability of the oil was investigated.

5.2 Materials and methods

5.2.1 General

Sterculia foetida L. oil originating from Indonesia was obtained from the Bandung Institute of Technology, Indonesia. Methanol (99.9%), diethyl ether (>99.0%), toluene (99.5%), dichloromethane (99.9%) were obtained from Lab-Scan (Gliwice, Poland). Heptane (>99%), cyclohexane (>99%), and sodium methoxide (anhydrous) were obtained from Acros Organics (Geel, Belgium). Dicyclopentadiene (93%) and 1-octene (>97%) were obtained from Merck (Darmstadt, Germany). Ammonium hydroxide solution (≥ 25% NH_3 in H_2O), trimethylsulfonium hydroxide (0.25 M in methanol), and tert-butylhydroperoxide solution (5.5 M in decane) were obtained from Fluka (Buchs, Switzerland). Palladium(II)acetate 98%, the tri-sodium salt of tris(m-sulfophenyl)phosphine (Na_3TPPTS) 96%, scandium(III)triflate 99%, copper(II)triflate 98%, Grubbs' 2nd generation catalyst ((1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(phenylmethylene) (tricyclohexyl phosphine) ruthenium), n-octylmagnesium bromide solution (2.0 M in diethylether), furan (98%), Al_2O_3 (basic, activated, Brockmann I, ~150 mesh, surface area 155 m^2/g), 2,3-dimethyl-2-butene (98%), 3-pyridinemethanol (98%), potassium-tert-butoxide solution (1 M in THF), tert-butyl methyl ether (98%), urea (98%), chloroform-d (99.8 atom %D), Fuller's earth (100-200 mesh), Quantofix® peroxide test sticks 1-100 mg/L, 2-amino-2-methyl-1-propanol (≥97%), and KF on alumina (40 %-wt loading) were obtained from Sigma-Aldrich (Steinheim, Germany). Aqueous hydrogen peroxide (30 wt%) and sodium chloride (>99.5%) were obtained from Merck (Darmstadt, Germany). Palladium on carbon (5 wt%) was obtained from Engelhard (Rome, Italy). Methyltrioxorhenium (MTO, 98%) and OsO_4 (FibreCat™ 3003) were obtained from Alfa Aesar (Sulzbach, Germany). Magnesium sulphate (dried) was from Boom BV (Meppel, The Netherlands). All materials were used as received unless otherwise stated.

5.2.2 Analytical methods

The ^{1}H, ^{13}C, and APT NMR spectra were recorded in $CDCl_3$ at room temperature using a Varian AS400 or AS200 NMR Spectrometer. For ^{1}H NMR spectra, a total of 32 scans were performed with a relaxation delay of 1 s while 4000 scans were recorded for ^{13}C and APT NMR spectra with a relaxation delay of 5 s.

Quantification and compositional analysis of the fatty acids were performed by GC using a Shimadzu 2014 model equipped with HP1 5973 column (length 30 m, inside diameter 0.25 mm, film 0.25 μm) and an FID detector. GC-MS spectra for structural analysis were recorded on an HP 6890 model equipped with the same column as the GC-FID and with a mass selective detector. Peak identification was done using the NIST05a mass spectra library. For both GC methods, injection and detection were performed at 280 °C, using oven temperature heating profiles from 175 to 280 °C with an increment of 8 °C/min. The STO was *trans*-methylated using trimethylsulfonium hydroxide solution prior to analysis by GC-MS and GC-FID according to a published procedure [31]. Typically, the oil (100 mg) was dissolved in methyl tert-butyl ether (5 mL). This solution (200 μL) was placed in a 2 mL vial

equipped with insert and trimethylsulfonium hydroxide (100 μL) was added and mixed, and the sample was injected to the GC.

The oxidation and rearrangement products were analysed by GC-MS after a derivatisation protocol using 2-amino-2-methyl-1-propanol, as described in [32]. The sample (up to 4 mg) was charged to a 4 mL vial and 2-amino-2-methyl-1-propanol (500 μL) was added. The tube was flushed with nitrogen, capped, and heated in oven at 180 ^{o}C for 18 h. After this period, the mixture was allowed to cool to RT. Dichloromethane (5 mL) and milli-Q water (2 mL) were added. The tube was shaken thoroughly and subsequently the organic and water phase were allowed to settle. The aqueous layer was removed using a pasteur pipette and the organic layer was washed again with water (2 mL). The organic layer was dried over $MgSO_4$. Dichloromethane was removed by a gentle N_2 stream. The sample was then dissolved in iso-octane and injected to the GC-MS.

The oxidation products were also analysed by GC-MS after a derivatisation protocol using pyridinemethanol, as described in ref. 33. Typically, 3-pyridinemethanol (400 μL) was mixed with potassium tert-butoxide solution (200 μL) to obtain a homogeneous solution. This mixture (500 μL) was mixed with the sample (10 mg) in dry dichloromethane (2 mL) in a 4 mL vial. The vial was closed and subsequently heated to 45 ^{o}C for 45 min. Thereafter, the mixture was allowed to cool to RT and water (2 mL) and hexane (4 mL) were added and the biphasic system was intensely mixed. The phases were allowed to settle and the organic phase was taken and washed with water (2 mL) and dried over $MgSO_4$. The solvents were removed by evaporation (200 mbar, 50 ^{o}C). The oily product was dissolved in hexane (1 mL) and injected to the GC-MS.

High resolution ESI-MS (HR-ESI-MS) analysis was performed using an EASY-nLC™ II HPLC apparatus from Proxeon Biosystems A/S, Denmark. The measurements were run in the positive scan mode with a sample concentration of 1 mg/mL in chloroform.

The cloud point (CP) and pour point (PP) analyses were determined using a Mini Pour/Cloud Point tester model MPC-102A/102L from Tanaka Scientific Limited, Tokyo, Japan, with detection interval of 1 ^{o}C. The L mode was used for STO and the UH mode for the modified oils and esters.

The acid value of the products was determined using a slightly modified acid-base titration procedure reported by the National Cottonseed Products Association (Method number 28.029). The product (0.1 g) was weighed, mixed with diethyl ether and ethanol (50/50%, v/v solution, 20 mL) and then titrated with a 0.01 N KOH solution in ethanol using phenolphthalein as the indicator until a faint red colour appeared and persisted for at least 30 seconds.

5.2.3 Purification of STO

For the olefin metathesis reaction, the oil was de-acidified using a procedure reported in [24(a)]. The oil was washed with aqueous NH_4OH solution at RT for 10 min. The soap was removed by centrifugation. Thereafter, the oil was washed several times with water and centrifuged (4000 rpm) until a clear oil was obtained. The

neutral oil was mixed with Fuller's earth at RT for 1 hour and centrifuged (4000 rpm) to remove the remaining solids. The oil was stored under nitrogen before the reaction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (m, -C***H***=C***H***-), 5.26 (m, OC***H***$(CH_2)_2$), 4.29 (dd, *J* = 11.9 Hz, 4.3 Hz, OCH(C***H***$_2)_2$), 4.14 (dd, *J* = 11.9 Hz, 6.0 Hz, OCH(C***H***$_2)_2$), 2.76 (t, *J* = 6.4 Hz, =CH-C***H***$_2$-CH=), 2.36 (t, *J* = 7.2 Hz, -C***H***$_2$COO-), 2.30 (3H, m, allylic -C***H***$_2$- of cyclopropene), 2.02 (1H, m, allylic -C***H***$_2$- of cyclopropene), 1.61 (m, -C***H***$_2$-), 1.57 – 1.33 (m, -C***H***$_2$-), 1.33 – 1.21 (m, -C***H***$_2$-), 0.87 (t, *J* = 6.8 Hz, C***H***$_3$CH$_2$), 0.76 (2H, s, -C-C***H***$_2$-C-, cyclopropene).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2-172.7 (-***C***OO-), 130.1-127.9 (***C***H=***C***H), 109.5-109.1 (-***C***-CH$_2$-***C***-, cyclopropene), 68.9 (O***C***H$(CH_2)_2$), 62.1 (OCH(***C***H$_2)_2$), 34.3-34.1 (allylic -***C***H$_2$- of cyclopropene), 31.9 (-***C***H$_2$-), 31.0 – 28.8 (-***C***H$_2$-), 27.5 – 26.9 (-***C***H$_2$-), 26.0 – 25.6 (-***C***H$_2$-), 24.8 (-***C***H$_2$-), 22.6 (-***C***H$_2$-), 14.1 (***C***H$_3$CH$_2$), 7.4 (-C-***C***H$_2$-C-, cyclopropene).

5.2.4 *Trans*-esterification of STO with methanol

The procedure for the *trans*-esterification reaction of STO with methanol was adapted from the work of Karaosmanoğlu *et. al.* [34]. Before *trans*-esterification, the oil was purified as follows: crude oil (15 mL), diethyl ether (15 mL), and $CaCO_3$ (2 g) were mixed at RT for 10 minutes, centrifuged, and decanted to obtain the organic phase. $MgSO_4$ (2 g) was added to the organic phase and mixed for 5 minutes, centrifuged, and decanted. The organic phase was then filtered through a 0.45 μm PTFE filter. Diethyl ether was removed by evaporation in a rotary evaporator (stepwise down to 20 mbar at 40 °C, few hours) and characterised by ^{1}H NMR to check the presence of remaining ether.

A pre-determined amount of purified STO (10 g, 11.2 mmol) was added to a solution of methanol (2.43 mL, 60 mmol) and sodium methoxide (0.34 mL, 30 vol% in methanol) in a flask (50 ml) at 35 °C. The mixture was allowed to react overnight, thereafter, an equal volume of water was added to allow separation in a centrifuge tube. The mixture was shaken once gently, therefore shaken vigorously two times and directly centrifuged. The upper phase was decanted and dried over $MgSO_4$ to obtain the methyl esters (STO FAME). The STO FAME (**1**) was characterised by ^{1}H, ^{13}C NMR and HPLC HR-ESI-MS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (m, C***H***=CH), 3.63 (m, COOC***H***$_3$), 2.74 (t, *J* = 6.0 Hz, =CH-C***H***$_2$-CH=), 2.34 (t, *J* = 6.8 Hz, -C***H***$_2$COO-), 2.27 (4H, t, *J* = 7.0 Hz, allylic -C***H***$_2$- of cyclopropene), 2.00 (1H, m, *J* = 7.0 Hz, allylic -C***H***$_2$- of cyclopropene), 1.59 (m, -C***H***$_2$-), 1.55 – 1.45 (m, -C***H***$_2$-), 1.40 – 1.17 (m, -C***H***$_2$-), 0.85 (t, *J* = 6.4 Hz, C***H***$_3$CH$_2$), 0.73 (2H, s, -C-C***H***$_2$-C-, cyclopropene).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1 (-***C***OO-), 130.0-129.6 (***C***H=***C***H), 127.9-127.8 (***C***H=***C***H), 109.5-109.1 (-***C***-CH$_2$-***C***-, cyclopropene), 51.3 (COO***C***H$_3$), 34.0 (allylic -***C***H$_2$- of cyclopropene), 31.8 (allylic -***C***H$_2$- of cyclopropene), 29.6 – 28.9 (-***C***H$_2$-), 27.3 – 27.1 (-***C***H$_2$-), 25.9 (-***C***H$_2$-), 25.6 (-***C***H$_2$-), 24.9 (-***C***H$_2$-), 22.6 (-***C***H$_2$-), 14.0 (***C***H$_3$CH$_2$), 7.3 (-C-***C***H$_2$-C-, cyclopropene).

HR-ESI-MS: *m/z* 295.2630 [C18:2, M + H]$^+$ (calc. 295.2639), 295.2630 [C18:CE, M + H]$^+$ (calc. 295.2639), 297.2789 [C18:1, M + H]$^+$ (calc. 297.2795), 309.2789 [C19:CE, M + H]$^+$ (calc. 309.2795).

5.2.5 Enrichment of the cyclopropene content in STO FAME

The cyclopropene content in the STO FAME was enriched by a fractionation method using urea [35]. The procedure was as follows: urea (20 g) was added to methanol (100 mL) and the mixture was heated at reflux until all urea was dissolved. STO FAME (8.3 g) as prepared in subsection 2.4 was added to the methanol solution, mixed, and allowed to cool to RT overnight. The resulting suspension was filtered and the remaining solids were washed twice with methanol (2.5 mL) saturated with urea. The solution was then poured into aqueous HCl (1%, 60 mL) and extracted twice, first with hexane (50 mL) then with diethyl ether (50 mL). The organic layers were combined and washed twice with water (50 mL) and subsequently dried over $MgSO_4$. The solvents were removed by evaporation in a rotary evaporator (200 mbar, 30 - 50 ^oC) for 2 hours. After removing the solvent, 3.0 g of methyl esters were recovered. The content of fatty acids with cyclopropene units was 81 %-mol as determined by GC-MS.

5.2.6 Modification reactions

The modification reactions were performed either using the STO FAME (Diels-Alder and rearrangement reactions) or the purified STO (olefin metathesis and oxidation – addition reactions), see Fig. 1 for details. In the latter case, the methyl esters were obtained after the modification reaction by a subsequent *trans*-esterification reaction with methanol.

5.2.6.1 Diels-Alder reactions of STO FAME with cyclopentadiene

The Diels-Alder reactions were carried out according to a procedure published by Corey and coworkers [36]. Cyclopentadiene was obtained from dicyclopentadiene by catalytic cracking using Cu metal. Dicyclopentadiene (10 g) was charged to a distillation set-up equipped with a Vigreux column containing copper. The cyclopentadiene vapor was collected in a condenser and cooled and stored in an ice bath (0 ^oC) to prevent dimerisation.

Typically, the Diels-Alder experiments were performed as follows: STO FAME, **1** (3 g, 10 mmol), as prepared in sub-section 5.2.4, were placed in an Erlenmeyer flask (100 ml) and the diene (cyclopentadiene or furan) was added at the desired mol ratio (1 or 15). Solvent (toluene, cyclohexane, or water; 10 mL) and in some cases a catalyst (10 mol%), were added and the reaction was carried out at the desired temperature (22, 30, and 40 ^oC) for 18 hours. The solvent and excess diene were removed by evaporation using a rotary evaporator (100 mbar, 80 ^oC) for 2 hours. Product (**2**) was characterised by ^1H and ^{13}C NMR.

^{1}H NMR (200 MHz, $CDCl_3$) δ 5.75 (2H, s, -CH-C***H***=C***H***-CH-, Diels-Alder adduct), 5.27 (m, -C***H***=C***H***-), 3.58 (s, COOC***H***$_3$), 2.69 (t, *J* = 5.3 Hz, =CHC***H***$_2$CH=), 2.49 (2H, s, -C-C***H***-CH=CH-C***H***-C-, Diels-Alder adduct), 2.24 (m, -C***H***$_2$COO-), 1.95 (m, -C***H***$_2$CH=CH-), 1.70 (1H, d, *J* = 6.0 Hz, CH-C***H***$_2$-CH, Diels-Alder adduct), 1.62 – 1.07 (m, -C***H***$_2$-), 0.79 (t, *J* = 5.7 Hz, C***H***$_3$CH$_2$), 0.45 (1H, d, *J* = 4.8 Hz, -C-C***H***$_2$-C, cyclopropane, Diels-Alder adduct), 0.0 (1H, m, -C-C***H***$_2$-C, cyclopropane, Diels-Alder adduct).

^{13}C NMR (50 MHz, $CDCl_3$) δ 175.5 (-***C***OO-), 133.2 (-CH-***C***H=***C***H-CH-, Diels-Alder adduct), 130.2 (***C***H=***C***H), 59.7 (CH-***C***H$_2$-CH, Diels-Alder adduct), 51.6 (COO***C***H$_3$), 47.9 (-C-***C***H-CH=CH-***C***H-C-, Diels-Alder adduct), 34.3 (-***C***H$_2$-), 32.1-31.8 (-***C***H$_2$-), 30.2 – 28.9 (-***C***H$_2$-), 27.9 (-***C***H$_2$-), 27.5 (-***C***H$_2$-), 25.2 (-***C***H$_2$-), 22.9 (-***C***H$_2$-), 14.3 (***C***H$_3$CH$_2$).

5.2.6.2 Olefin metathesis reactions of STO with 2,3-dimethyl-2-butene

Olefin metathesis reactions were performed using a procedure given by Mol [37]. The syntheses were carried out under nitrogen using standard Schlenk and glovebox techniques. STO (2 g, 2.23 mmol) was added to a Schlenk tube containing Grubbs' 2nd generation catalyst, (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro (phenylmethylene) (tricyclohexylphosphine) ruthenium (10 mg, $1.18.10^{-5}$ mol) and the mixture was stirred at RT. The olefin (2,3-dimethyl-2-butene) was introduced (olefin to cyclopropene mol ratio of 20:1) and the resulting mixture was kept at 55 ^{o}C for 6 hours. Thereafter, the mixture was cooled to RT and the olefin was removed by evaporation using a rotary evaporator (100 mbar, 80 ^{o}C) for 2 hours. Subsequently, the mixture was added over a silica gel column to remove catalyst residues, giving product **3a**. Thereafter, a *trans*-esterification with methanol was performed under reaction conditions as described in sub-section 5.2.4. The product, **4a**, was characterised using ^{1}H and ^{13}C NMR.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (s, =C***H***), 5.54 (s, =C***H***), 5.34 – 5.14 (m, C***H***=C***H***), 4.84 (s, C***H***=C***H***), 4.83 (s, -C***H***=C***H***-), 4.77 (m, C***H***=C***H***), 4.60 (m, C***H***=C***H***) 3.50 (s, COOC***H***$_3$), 2.50 (t, *J* = 7.4 Hz, $(CH_3)_2$C=C-C***H***$_2$-C=C$(CH_3)_2$, metathesis adduct and linoleic derivatives), 2.14 (t, *J* = 7.4 Hz, -C***H***$_2$COO-), 1.85 (m, (***H***$_2$C-$(CH_3)_2$C=C-CH$_2$-C=C$(CH_3)_2$-C***H***$_2$, allylic, metathesis adduct and unsaturated fatty acid (derivatives)), 1.66 (m, C=C(C***H***$_3$)$_2$, metathesis adduct), 1.65 (m, C=C(C***H***$_3$)$_2$, metathesis adduct), 1.48 (s, C=(C***H***$_3$)$_2$, metathesis adduct), 1.46 (m, -C***H***$_2$-), 1.26 – 0.79 (m, -C***H***$_2$-), 0.72 (t, *J* = 6.6 Hz, C***H***$_3$CH$_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5-174.3 (-***C***OO-), 133.8 (***C***=***C***), 130.6-128.0 (***C***=***C***), 118.2 (***C***=***C***), 51.6 (COO***C***H$_3$), 34.3 – 27.2 (-***C***H$_2$-), 25.2 (-***C***H$_2$-), 22.9 (-***C***H$_2$-), 14.3 (***C***H$_3$CH$_2$).

5.2.6.3 Olefin metathesis reactions of STO with 1-octene

Olefin metathesis reaction with 1-octene to give **3b** and the subsequent *trans*-esterification to yield **4b** were performed at similar conditions as given for 2,3-dimethyl-2-butene. The reaction mixture after *trans*-esterification was analysed by ^{1}H, ^{13}C NMR, and HPLC HR-ESI-MS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (d, *J* = 4.4 Hz, =C***H***$_n$), 5.64 (d, *J* = 6.0 Hz, =C***H***$_2$), 5.47 – 5.17 (m, C***H***=C***H***), 4.94 (m, C=C***H***-, metathesis adduct), 4.86 (m, C=C***H***$_2$, metathesis adduct), 4.73 – 4.68 (m, C***H***=C***H***), 3.61-3.60 (m, COOC***H***$_3$), 2.61 (dd, *J* = 7.1 Hz, =C-C***H***$_2$-C=, metathesis adduct or linoleic acid derivative), 2.24 (m, -C***H***$_2$COO-), 2.15-1.85 (m, allylic -C***H***$_2$-, remaining cyclopropene), 2.05 – 1.0 (m, -C***H***$_2$-), 0.83 (t, *J* = 5.6 Hz, C***H***$_3$CH$_2$), 0.71 (m, C-C***H***$_2$-C, remaining cyclopropene).

HR-ESI-MS: *m/z* 407.3871 [C18:CE metathesis adduct, M + H]$^+$ (calc. 407.3891), 421.4040 [C19:CE metathesis adduct, M + H]$^+$ (calc. 421.4047).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5 (***C***OO-),114.3 (***C***H=***C***H), 112.6-112.4 (***C***H=***C***H), 51.6 (COO***C***H$_3$), 34.0 (allylic ***C***H$_2$-C= cyclopropene), 32.1-31.9 (allylic ***C***H$_2$-C= cyclopropene), 29.9-29.0(-***C***H$_2$-), 27.6-27.4 (-***C***H$_2$-), 26.3-26.2 (-***C***H$_2$-), 25.2 (-***C***H$_2$-), 22.9-22.8 (-***C***H$_2$-), 14.3 (***C***H$_3$CH$_2$), 7.6 (C-***C***H$_2$-C, remaining cyclopropene).

5.2.6.4 Oxidation of STO at typical epoxidation conditions using the Sharpless method [38]

MTO ($4.78.10^{-2}$ g, 0.14 mmol), pyridine (279 μL, 3.5 mmol), STO (10 g, 28.8 mmol total C=C), and dichloromethane (5.8 mL) were placed in a three necked round bottom flask equipped with a reflux condenser. The reaction was started by the drop wise addition of aqueous hydrogen peroxide (6.0 mL, 57.6 mmol) under vigorous stirring at RT in about 10 min. The stirring was stopped after 1.5 h and subsequently diethyl ether (150 mL) and brine (100 mL) were added and both liquid phases were allowed to settle. The organic phase was passed through a basic Al_2O_3 column to remove catalyst residues, subsequently washed with brine until no peroxide was left and dried over $MgSO_4$. The solvents were removed under vacuum (150 mbar, 30 ^{o}C) for 3 hours. The product (**5**) was characterised using NMR (^{1}H, ^{13}C) and GC-MS after derivatisation with pyridinemethanol and 2-amino-2-methyl-1-propanol. Subequently, **5** was *trans*-esterified with methanol and the methyl esters were characterised using APT and HPLC HR-ESI-MS.

^{1}H NMR for **5**: (201 MHz, $CDCl_3$) δ 5.93 (1H, s, O=C-C=C***H***$_2$, unsaturated ketone), 5.67 (1H, s, O=C-C=C***H***$_2$, unsaturated ketone), 5.28 (s, remaining -C***H***=C***H***-), 5.26 (m, OC***H***(CH$_2$)$_2$), 4.28 (dd, *J* = 12 Hz, 4.4 Hz, OCH(C***H***$_2$)$_2$), 4.11 (dd, *J* = 12.0 Hz, 5.8 Hz, OCH(C***H***$_2$)$_2$), 3.15 – 2.79 (m, -C***H***-O-C***H***-, epoxide), 2.63 (t, *J* = 7.4 Hz, -C***H***$_2$COO-) , 2.41 – 2.10 (m, -C***H***$_2$-), 1.65-1.12 (m, -C***H***$_2$-), 0.85 (t, *J* = 6.2 Hz, C***H***$_3$CH$_2$).

^{13}C NMR for **5**: (50 MHz, $CDCl_3$) δ 202.5 (O=***C***-C=CH_2, unsaturated ketone), δ 202.4 (O=***C***-C=CH_2, unsaturated ketone), 173.2-172.8 (-***C***OO-), 149.0 (O=C-***C***=CH_2, unsaturated ketone), 148.9 (O=C-***C***=CH_2, unsaturated ketone), 123.5 (O=C-C=***C***H_2, unsaturated ketone), 123.4 (O=C-C=***C***H_2, unsaturated ketone), 68.9 (-O***C***H$(CH_2)_2$), 62.1 (OCH(***C***$H_2)_2$), 57.2 (-***C***H-O-***C***H-, epoxide), 37.8 (-***C***H_2-), 37.7 (-***C***H_2-), 34.1- 22.6 (-***C***H_2-), 14.1 (***C***H_3CH_2).

APT NMR for methyl esters of **5** (101 MHz, $CDCl_3$) δ 202.7 and 201.9 (O=***C***-C=CH_2, upward, unsaturated ketone), 174.2 and 173.9 (-***C***OO-, upward), 149.2 and 148.9 (O=C-***C***=CH_2, upward, unsaturated ketone), 123.1 and 122.8 (O=C-C=***C***H_2, upward, unsaturated ketone), 57.2-56.5 (-***C***H-O-***C***H-, downward, epoxide), 51.3 (COO***C***H3, downward), 37.7-37.6 (-***C***H_2-, upward), 34.1-33.8 (-***C***H_2-, upward), 32.0 – 31.7 (-***C***H_2-, upward), 30.8-30.7 (-***C***H_2-, upward), 29.9 – 28.1 (-***C***H_2-, upward), 27.9 – 25.8 (-***C***H_2-, upward), 26.8 – 23.7 (-***C***H_2-, upward), 22.5 (-***C***H_2-, upward), 14.1 (***C***H_3CH_2, downward).

HR-ESI-MS for methyl esters of **5**: *m/z* 311.2582 [C18 enone, M + H]$^+$ (calc. 311.2588), 313.2736 [epoxystearate, M + H]$^+$ (calc. 313.2744), 325.2738 [C19 enone, M + H]$^+$ (calc. 325.2744), 327.2528 [diepoxystearate, M + H]$^+$ (calc. 327.2537).

5.2.6.5 Oxidation of STO at typical dihydroxylation conditions using the Prilezhaev method [39]

STO (10 g, 28.8 mmol total C=C) and formic acid (8.7 mL, 230 mmol) were placed in a three necked round bottom flask. The reaction was started by the dropwise addition of aqueous hydrogen peroxide (6.0 mL, 57.6 mmol) at RT over a period of 10 min and the mixture was allowed to react under vigorous stirring. After 24 h, stirring was ceased and diethyl ether (150 mL) and brine (100 mL) were added. After vigorous mixing, both liquid layers were allowed to settle. The organic phase was washed with brine until no residual peroxide could be detected and dried over $MgSO_4$. The solvent was removed in vacuo (300 mbar, 30 ^{o}C) for 1 h. The product (**6**) was characterised using ^{1}H and ^{13}C NMR and GC-MS after derivatisation with pyridinemethanol.

^{1}H NMR (201 MHz, $CDCl_3$) δ 8.16-8.0 (m, CH-O-C***H***O, formyl branch), 5.94 (1H, s, O=C-C=C***H***$_2$, unsaturated ketone), 5.67 (1H, s, O=C-C=C***H***$_2$, unsaturated ketone), 5.24 (m, OC***H***$(CH_2)_2$), 4.68 (m, C***H***-O-CHO, formyl branch), 4.28 (dd, *J* = 11.8 Hz, 4.0 Hz, OCH(C***H***$_2)_2$), 4.12 (dd, *J* = 11.7 Hz, 5.8 Hz, OCH(C***H***$_2)_2$), 3.95-3.35 (m, HO-C***H***-C***H***-OH, dihydroxy), 2.64 (m, -C***H***$_2$COO-), 2.27 (m, -C***H***$_2$-), 1.74 – 1.06 (m, -C***H***$_2$-), 0.86 (t, *J* = 6.5 Hz, C***H***$_3CH_2$).

^{13}C NMR (50 MHz, $CDCl_3$) δ 202.5 and 202.4 (O=***C***-C-CH_2, unsaturated ketone), 173.2 and 172.8 (-***C***OO-), 163.3 (CH-O-***C***HO, formyl branch), 149.0 and 148.9 (O=C-***C***-CH_2, unsaturated ketone), 123.5 and 123.4 (O=C-C-***C***H_2, unsaturated ketone), 75.4-72.0 (-***C***(H)OH-), 68.8 (-O***C***H$(CH_2)_2$), 62.0 (OCH(***C***$H_2)_2$), 57.5-56.7 (-***C***H-O epoxide), 37.8-37.7 (-***C***H_2-), 34.2-22.4 (-***C***H_2-), 14.1 (***C***H_3CH_2).

5.2.6.6 Addition reactions of 9(10)-ene-10(9)-oxo-octadecanoate with n-octyl magnesium bromide

The reaction of the 9(10)-*ene*-10(9)-oxo-octadecanoate moieties in **5** (section 2.6.4) with n-octylmagnesium bromide is based on the work of Tawney [40]. Typically, n-octylmagnesiumbromide solution (16.5 mL, 33 mmol, 2.0 M in diethyl ether) was mixed with $CuCl_2$ ($7.4.10^{-2}$ g, 0.55 mmol) in a three necked round bottom flask equipped with a reflux condenser at room temperature under N_2 for 45 min. The dispersion was cooled to 5 ^oC and then **5** (10 g, 27.5 mmol enone) dissolved in diethyl ether (15 mL) was added stepwise in a 1 hour period. Thereafter the reaction temperature was raised to 55 ^oC and the mixture was reacted for another 3 hour. The reaction mixture was allowed to stand overnight. Chipped ice (16.5 g) and glacial acetic acid (5 mL) were added to quench the reaction. Subsequently, diethyl ether (50 mL) was added and the water phase was separated from the organic phase. The water phase was washed with an equal volume of diethyl ether and the ether phase was combined with the organic phase. The resulting organic phase was dried over $MgSO_4$. The solvents were removed in vacuo (150 mbar, 30 ^oC for 1 hour, thereafter 30 mbar and 80 ^oC). The product (**7**) was characterised by ^1H and ^{13}C NMR.

^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (1H, s, O=C-C=C$\boldsymbol{H}_2$, remaining unsaturated ketone), 5.68 (1H, s, O=C-C=C$\boldsymbol{H}_2$, remaining unsaturated ketone), 5.25 (m, OC$\boldsymbol{H}$(CH_2)$_2$), 5.03-4.9 (s, C=C$\boldsymbol{H}_2$, (1+2)-addition adduct), 4.28 (m, OCH(C$\boldsymbol{H}_2$)$_2$), 4.13 (dd, J = 11.1 Hz, 5.6 Hz, OCH(C$\boldsymbol{H}_2$)$_2$), 3.63 (m, C$\boldsymbol{H}$-OH, hydroxy), 2.64 (m, C$\boldsymbol{H}$, (1+4)-addition adduct), 2.31 (t, J = 7.4 Hz, -C$\boldsymbol{H}_2$COO-), 1.7-1.1 (m, -C$\boldsymbol{H}_2$-), 0.87 (t, J = 5.8 Hz, C$\boldsymbol{H}_3$$CH_2$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216-211 (O=$\boldsymbol{C}$-CH, (1+4)-addition adduct), 174.0-172.5 (-$\boldsymbol{C}$OO-), 152.9 (CH_2=$\boldsymbol{C}$-C-OH, (1+2)-addition adduct), 108.1 ($\boldsymbol{C}$$H_2$=C-C-OH, (1+2)-addition adduct), 78.0 ($\boldsymbol{C}$H-OH), 74.4 ($\boldsymbol{C}$H-OH), 72.9 (CH_2=C-$\boldsymbol{C}$-OH, (1+2)-addition adduct), 68.8 (O$\boldsymbol{C}$H(CH_2)$_2$), 63.0-62.1 (OCH($\boldsymbol{C}$$H_2$)$_2$), 54.0-50.5 (CH (1+4)-addition adduct), 43.0-22.5 (-$\boldsymbol{C}$$H_2$-), 14.1 ($\boldsymbol{C}$$H_3$$CH_2$).

5.2.6.7 Rearrangement reactions of STO FAME

The rearrangement reaction of STO FAME (**1**) was performed using Pd-TPPTS and Pd/C in heptane or cyclohexane as solvent, according to a procedure reported by Kai and Pryde [16]. The reactions were carried out in a stirred batch stainless steel autoclave (350 ml, Buchii GmBH) under nitrogen using a stirrer speed of 1400 rpm. Typically, **1** (3 g, 10 mmol), as prepared in sub-section 2.4., were charged to the autoclave and dissolved in 100 ml of an organic solvent (heptane or cyclohexane). In the case of the homogeneous Pd-TPPTS catalyst, water was added (volume ratio of water to organic solvent was 1 or 0.5). Subsequently, the heterogeneous catalyst (Pd/C) or the homogeneous catalyst components, (Pd-acetate, 0.5%-w on ester, calculated as metal and TPPTS ligand at a molar ratio of ligand to metal precursor of 2) were added. The reactor was flushed with nitrogen, closed, and the reactor contents were heated to the pre-determined temperature (90 ^oC for the homogeneous catalyst and 150 ^oC for Pd/C). A typical reaction time of 6 h was applied. The reactor content was cooled to room temperature and the liquid phase was allowed to settle. The organic phase was collected and the solvent was removed

in vacuo at elevated temperature (212 mbar, 60 °C) for 2 hours. The product (**9**) was characterised by ^{1}H, APT ^{13}C-NMR and HPLC HR-ESI-MS.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 – 6.40 (m, C***H***=C***H*,** rearrangement product), 6.05 - 5.92 (m, C***H***=C***H*,** rearrangement product), 5.79 – 5.58 (m, C***H***=C***H*,** rearrangement product), 5.39-5.24 (m, C***H***=C***H*,** oleic and linoleic), 4.85 and 4.71 (m, =C***H*$_2$,** methylene branch, rearrangement product), 3.63-3.60 (s, COOC***H***$_3$), 2.75 (m, =CH-C***H***$_2$-CH=), 2.36-2.18 (m, -C***H***$_2$COO-), 2.08 – 1.11 (m, -C***H***$_2$-), 0.84 (t, *J* = 6.6 Hz, C***H***$_3$CH$_2$).

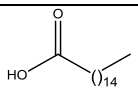
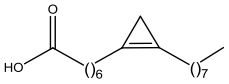
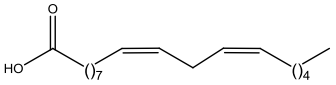
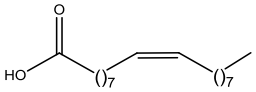
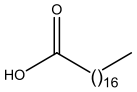
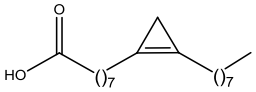
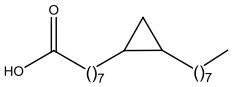
APT NMR (101 MHz, $CDCl_3$) δ 174.6 and 174.8 (-***C***OO-, upward), 147.0 and 146.9 (CH$_2$=***C***-CH=CH-, upward, rearrangement product), 132.7-128.4 (CH=***C***H, downward, rearrangement product and other unsaturated fatty acids), 113.4 and 113.3 (***C***H$_2$=C-CH=CH-, upward, rearrangement product), 51.3 (COO***C***H$_3$, downward), 35.0-20.3 (-***C***H$_2$-, upward), 14.6 (***C***H$_3$CH$_2$, downward).

HR-ESI-MS: *m/z* 295.2630 [C18:2, M + H]$^+$ (calc. 295.2639), 295.2630 [C18:2 conjugated, M + H]$^+$ (calc. 295.2639), 297.2786 [C18:1, M + H]$^+$ (calc. 297.2795), 309.2788 [C19:2 conjugated, M + H]$^+$ (calc. 309.2795).

5.3 Results and discussion

The modification reactions of STO in this study are primarily aimed to obtain branched ester derivatives of STO. The introduction of branches in the fatty acids chain of STO or its methyl esters (STO FAME) were performed by various modification reactions. Synthetic strategies include Diels-Alder, olefin metathesis, oxidation, addition, and rearrangement reactions, as summarised in Fig. 1. As the STO contains also considerable amounts of saturated and unsaturated fatty acids (up to 33 wt%, see Table 1), the products of the modification reactions are mixtures of cyclopropene derived products and straight chain fatty acids or derivatives thereof. Product separation by conventional methods (distillation, extraction) proved very cumbersome. The product mixtures as such were therefore analysed by NMR (^{1}H, ^{13}C, APT), HPLC HR-ESI-MS and in some cases with GC-MS using suitable derivatisation strategies to determine the chemo- and regio-selectivity of the reactions involving the cyclopropene units.

Table 1 Fatty acids composition of STO

Fatty acids			This study (GC-FID, wt%)	Literature [5] (wt%)
Palmitic acid	C16:0		17.1	20.0
Malvalic acid	C18:CE		9.1	11.4
Linoleic acid	C18:2		5.6	4.12
Oleic acid	C18:1		7.4	8.3
Stearic acid	C18:0		2.1	0.54
Sterculic acid	C19:CE		58.2	55.7
Dihydrosterculic acid	C19:CA		0.5	-
Total cyclopropenoid fatty acids fraction			**67.3**	**67.1**
Total unsaturated fatty acids fraction			**80.3**	**79.5**

5.3.1 Characterisation of the STO feedstock

Both the crude and purified STO were characterised using ^{1}H and ^{13}C NMR as well as GC-FID to determine the fatty acid composition and the CPEFA content of the oil. The ^{1}H and ^{13}C NMR spectra of the purified STO are shown in Fig. 2. Characteristic resonances of the cyclopropene units are present as a singlet at δ 0.76 ppm (C-C***H***$_2$-C) in ^{1}H NMR spectra and at δ 7.34 ppm (C-***C***H$_2$-C) and about 109 ppm (***C***-CH$_2$-***C***) in ^{13}C NMR. The conversion of the cyclopropene rings in the various reactions is easily monitored by ^{1}H NMR by considering the disappearance of the characteristic CH_2 resonances of the cyclopropene unit. In addition, the anticipated peaks of the glycerol backbone and fatty acid chains without cyclopropene units are present. The fatty acids composition according to GC-FID is presented in Table 1. The STO used in this study contains about 67 wt% of CPEFA, with sterculic acid as the main fatty acid in the triglyceride (58 wt%). Malvalic acid, the C18 derivative of sterculic acid, was present in much lower amounts (about 9 wt%. The fatty acid composition is in line with earlier literature data [5].

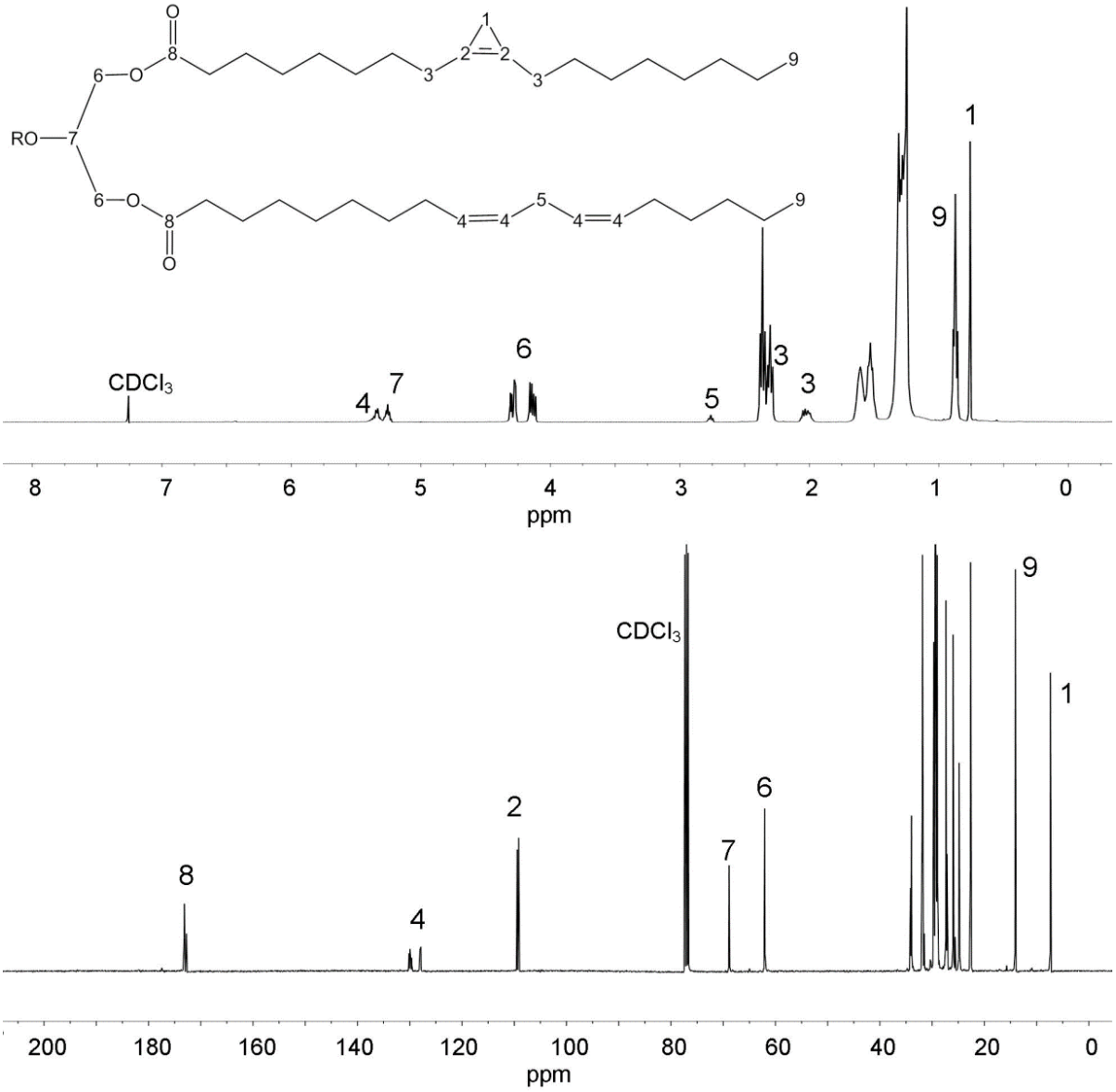


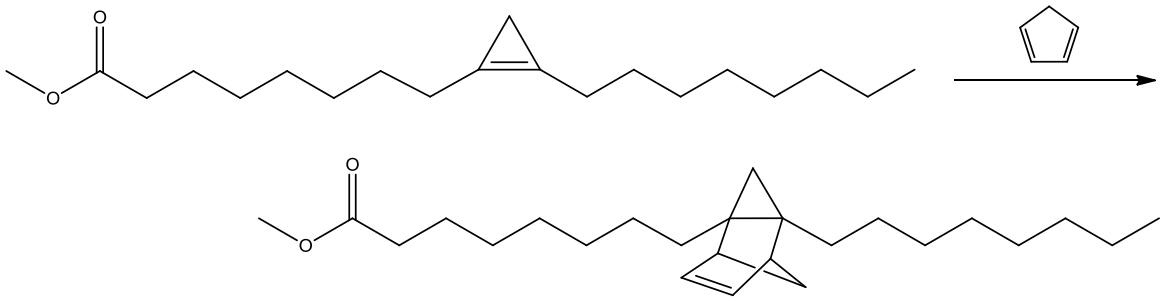
Fig. 2 ^{1}H and ^{13}C NMR spectra of STO

The acid value of the crude STO was 3.62 mg KOH/g oil. A significant reduction in the free fatty acid content was obtained by using a conventional de-acidification procedure (0.17 mg KOH/g oil). During this procedure, the cyclopropene content of the oil was not affected, an indication that the cyclopropene rings are stable in a basic environment.

The oil is easily converted to the corresponding methyl esters (FAME) by a conventional *trans*-esterification reaction with methanol at 35 °C using NaOMe as the basic catalyst. An HPLC HR-ESI-MS analysis (positive mode) of the STO FAME showed product peaks with *m/z* values of 309.2789 and 295.2630 amu, which correspond to methyl sterculate and methyl malvalate chains, respectively.

5.3.2 Diels-Alder reaction of STO FAME with cyclopentadiene

Diels-Alder reactions of the STO FAME (**1**) with cyclopentadiene were investigated to produce esters derivatives of STO with relatively bulky and unsaturated substituents in the fatty acid chains (eq 5). The reactions were performed in an apolar organic solvent (toluene/hexane) or water in a temperature range of 20-40 ^{o}C. In some cases, a typical Lewis acid catalyst like $Sc(OTf)_3$ or $Cu(OTf)_2$ was applied. An overview of the experiments is given in Table 2. Initial experiments were performed in toluene at RT with a 15 fold excess of cyclopentadiene on cyclopropene units for an 18 h reaction times. The cyclopropene conversion was 72 mol% in this case, and the selectivity to the anticipated Diels-Alder product was 93 mol% (eq. 5). By products were not identified.



(eq. 5)

In a subsequent experiment, the molar ratio of the cyclopentadiene to cyclopropene units was reduced from 15 to 1 to a 1 to 1 ratio. A considerable reduction in both the conversion and selectivity were observed (Table 2). However, when increasing the temperature from 20 to 40 ^{o}C, this negative effect may be suppressed and a high cyclopropene conversion and product selectivity were observed (86 and 93 mol%, respectively).

To reduce reaction times, the use of Lewis acid catalysts ($Sc(OTf)_3$ and $Cu(OTf)_2$) were explored. Full conversion of the cyclopropene rings was observed, however, the corresponding cycloaddition product was not observed (NMR). So far, we have not been able to identify the reaction products. Thus, Lewis acid catalysts indeed have a positive effect on activity, though do not lead to the formation of the desired products.

Table 2 Overview of the Diels-Alder reactions[a)]

Exp	Diene	T [°C]	Diene / dieno-phile [mol]	Solvent	Conversion [%-mol][b)]	Selectivity [%-mol][b)]
1	Cyclopentadiene	20	15	Toluene	72	93
2	Cyclopentadiene	20	1	Toluene	41	73
3	Cyclopentadiene	40	1	Toluene	86	93
4	Cyclopentadiene	20	1	Cyclohexane	46	66
5	Furan	20	15	Toluene	2	0
6	Cyclopentadiene	30	1	Toluene	70	92
7 [c)]	Cyclopentadiene	40	1	Toluene	>99	0
8 [d)]	Cyclopentadiene	40	1	Toluene	>99	0
9	Cyclopentadiene	40	1	Water	>99	>99

[a)]Reaction time: 18h; [b)]conversion and product selectivity were calculated by ^{1}H NMR. Conversion is the cyclopropene conversion, selectivity is defined as the amount of the Diels Alder product divided by the amount of cyclopropene rings converted. [c)]in presence of $Sc(OTf)_3$ [d)]in presence of $Cu(OTf)_2$

Solvent effects were explored by performing also some reactions in water and cyclohexane at 40 °C and a 1 to 1 mol ratio of cyclopentadiene and cyclopropene units. The results are given in Table 2. The differences in reaction performance between toluene and cyclohexane are only minor. The solubility parameter of toluene (8.9 $(cal/cm^3)^{0.5}$) and cyclohexane (8.2 $(cal/cm^3)^{0.5}$) [41] are close and as such no major differences are anticipated and this indeed proved to be the case. A reaction in water (40 °C, 18 hours, molar ratio of diene to dienophile = 1) gave excellent results. Essential quantitative cyclopropene conversion and selectivity to the cycloaddition product were observed (Table 3 entry 9). These findings are in line with extensive work by Breslow [42], who demonstrated that Diels-Alder reactions between non-polar compounds may proceed at much higher rates in water than in organic solvents. The reaction rate acceleration in water is probably due to favourable hydrogen bonding between water molecules and the polarised transition state [43,44].

A representative ^{1}H NMR spectrum of the cycloaddition product is shown in Fig. 3. Characteristic peaks of the cycloaddition products are at 0.0 and 0.45 ppm, belonging to the two diastereotopic protons of the cyclopropane CH_2 group, at 2.49 ppm (CH at the bridgehead) and 5.75 ppm (olefinic CH groups in the cycloaddition product). For comparison, ^{1}H NMR spectra of the oil of the *Litchi chinensis* plant, known to contain fatty acid chains with cyclopropane units, show resonances at δ -0.3 and 0.6 ppm for the methylene protons of the cyclopropane ring [45]. Based on the NMR data, only one of the possible geometric isomers is formed. Diels-Alder reactions are known to be concerted reactions, meaning that the new σ-bonds between the cyclopropene ring and cyclopentadiene are formed while the existing π-bonds are converted [46]. Based on this mechanism, the likely cycloaddition product is the *cis*-isomer.

Finally, also a reaction was performed with furan instead of cyclopentadiene (Table 2, entry 5). Disappointing results were obtained, a low conversion (2 mol%) and no indication for the formation of the cycloaddition product. These findings may be rationalised by considering that Diels-Alder reactions between an electron rich diene such as a furan are generally only successful with electron poor cyclopropenes, such as halo-substituted cyclopropenes [47].

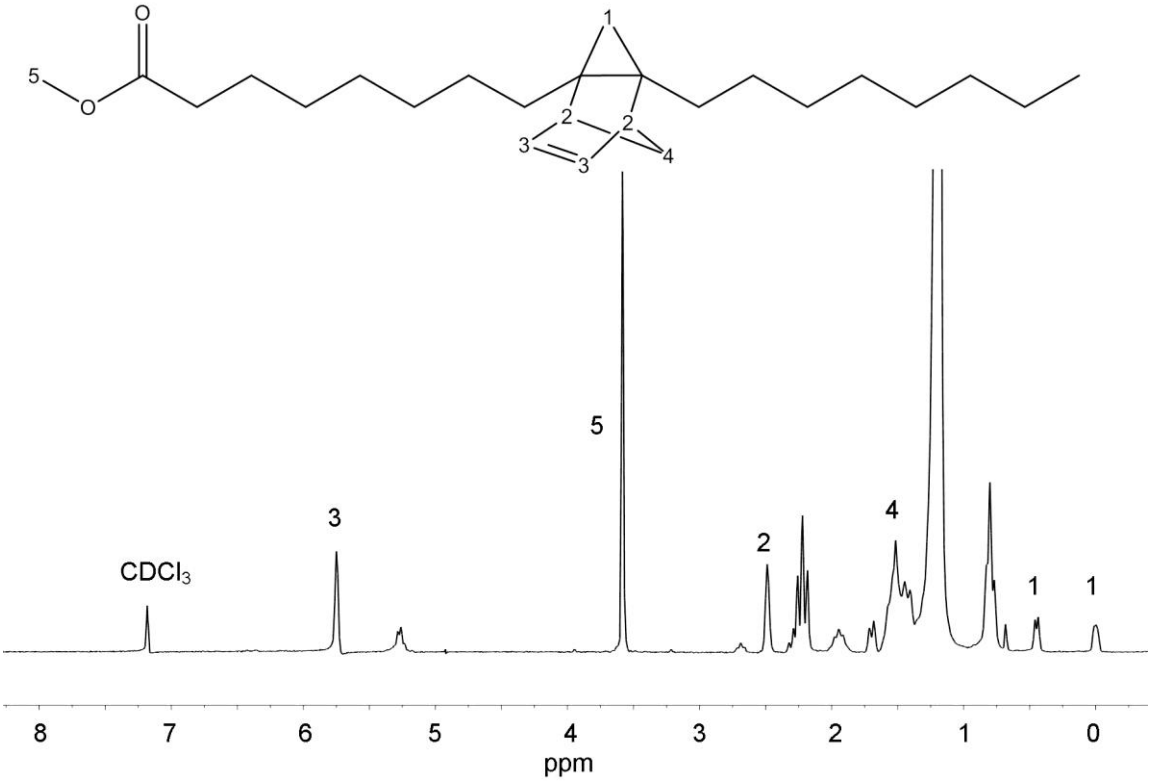
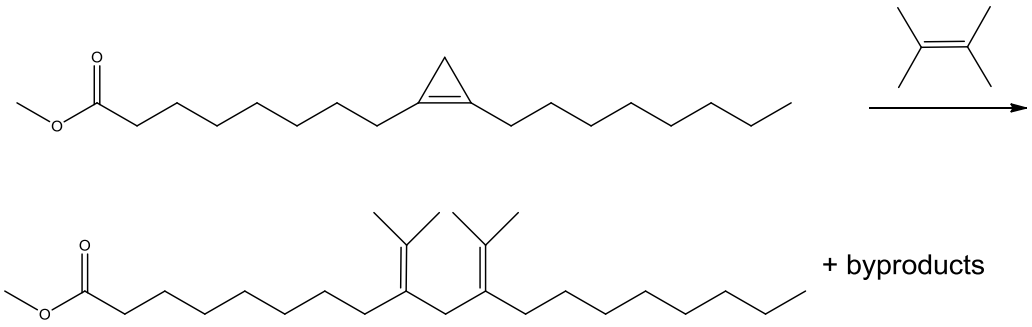


Fig. 3 ^{1}H NMR spectrum of Diels-Alder product of STO FAME (**2**) with cyclopentadiene

5.3.3 Olefin metathesis reactions of STO FAME with 2,3-dimethyl-2-butene or 1-octene

Cross olefin metathesis reactions of STO FAME, **1**, with aliphatic olefins (2,3-dimethyl-2-butene or 1-octene) were investigated as an alternative reaction to produce branched esters derivatives (eq 6). Grubbs' 2nd generation catalyst ((1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene) dichloro(phenylmethylene) (tricyclohexyl phosphine)(ruthenium) was used. Typical reaction times were 6 h and reaction temperature was either 40 or 55 ^{o}C. The olefin was used in excess on the cyclopropene units; the catalyst intake was 0.18 %-mol on cyclopropene units.



(eq. 6)

Initially, experiments were carried out with 2,3-dimethyl-2-butene at 40 °C (eq 6). Cyclopropene conversion was 78 mol% and the selectivity to the desired cross metathesis product was about 29 mol% (Table 3). Methyl branches of the cross metathesis products were observed by ^{1}H NMR by the appearance of sharp peaks in the regions δ 1.48-1.67 and 2.48-2.53 ppm (Fig. 4).

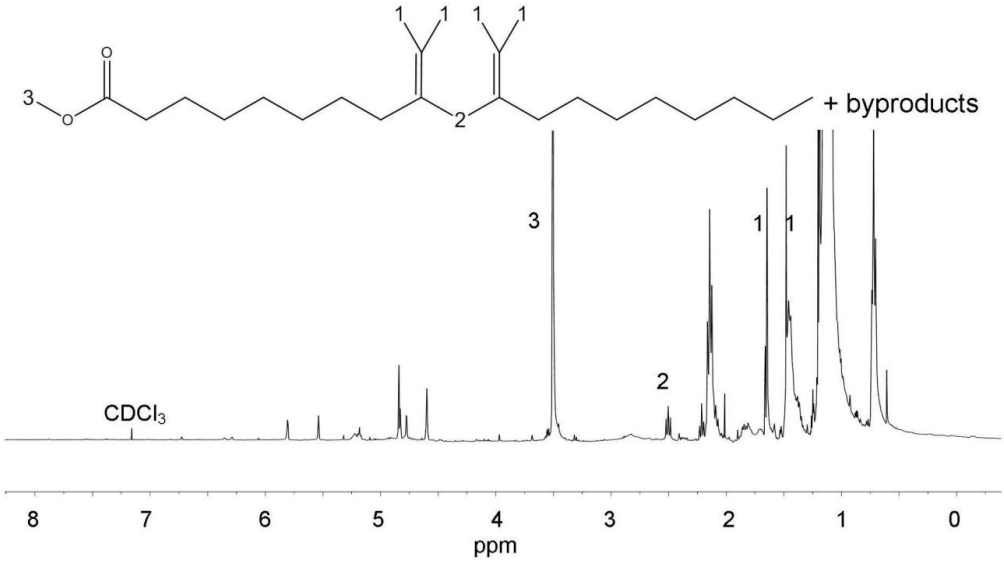


Fig. 4 ^{1}H NMR spectrum of the olefin metathesis reaction product of STO with 2,3-dimethyl-2-butene after *trans*-esterification with methanol (**4a**)

The selectivity of the reactions is relatively low, as the primary cross metathesis products are known to be prone to secondary or further metathesis reactions, giving rise to a broad spectrum of products [37,48]. In addition, the STO FAME do not only contain fatty acid chains with cyclopropene units but also the conventional mono- and di-saturated fatty acids like oleic and linoleic acid (see Table 1) that are also known to be reactive in metathesis reactions.

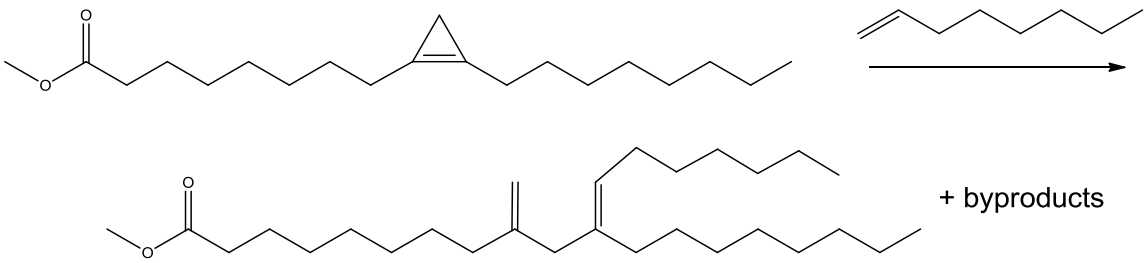
Experiments at slightly higher temperatures (55 instead of 40 °C), gave essential quantitative conversion of 2,3-dimethyl-2-butene and a selectivity to the desired branched fatty acid chains (eq 6) of 32 mol% (Table 3).

Table 3 Results of the olefin metathesis reactions[a)]

Exp	Olefin	Catalyst [%-mol]	Temp [°C]	Reaction time (h)	Conversion [%-mol]	Selectivity [%-mol]
1	2,3-dimethyl-2-butene	0.18	40	6	78	29
2	2,3-dimethyl-2-butene	0.18	55	6	99	32
3	1-octene	0.18	55	6	54	47
4	CPFA methyl ester	0.18	55	6	26	-
5	CPFA methyl ester	0.9	55	170	40	-

[a)]Conversion and product selectivity were calculated by ^{1}H NMR. Conversion is the cyclopropene conversion, selectivity is defined as the amount of the metathesis products divided by the amount of cyclopropene rings converted

Subsequent experiments were performed with 1-octene (eq 7). At 50 °C, 54 mol% cyclopropene conversion was observed after 6 h (Table 3). Like with 2,3-dimethyl-2-butene, the selectivity is rather low (47 mol%), likely due to consecutive reactions. For example, we also observed the formation of 10-methyl-9-undecenoic acid and 2-methyl-2-undecene (GC-MS), the reaction products of the oleic acid chains in STO with 2,3-dimethyl-2-butene. The presence of the branches was confirmed by ^{1}H NMR spectra, showing resonances of the $=CH_2$ groups of the methylidene branch at δ 4.86 ppm and at δ 4.94 ppm for the H atom of the =CHR unit of the C7 branch (eq. 7). An HPLC HR-ESI-MS analysis (positive mode) of the metathesis product showed product peaks with *m/z* values of 421.4040 and 407.3871 amu, which correspond to the metathesis product of 1-octene with methyl sterculate and methyl malvalate, respectively. The formation of these products was further confirmed by an oxidative cleavage experiment using OsO_4 as the catalyst and hydrogen peroxide as the oxidant in acetonitrile. The reaction mixture was analysed by GC-MS and clearly showed the presence of methyl 9,11-dioxononadecanoate, methyl 8,10-dioxooctadecanoate, heptanal, and heptanoic acid. This supports the formation of the cross-metathesis product with the C7 branch in the fatty acid chain.



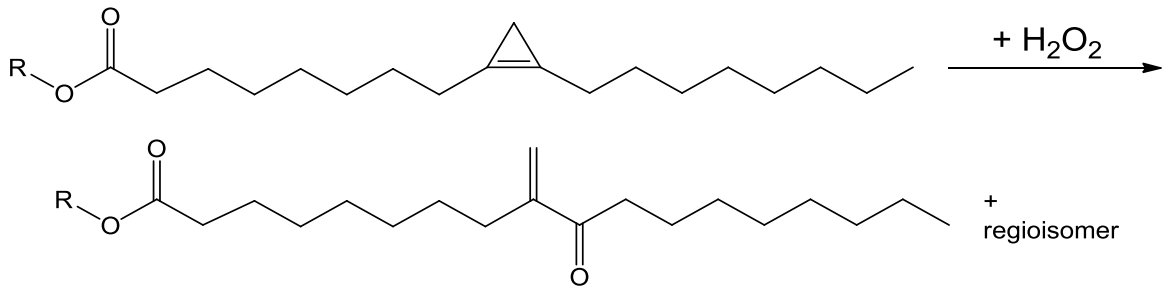
(eq. 7)

To gain insights in the reactivity of STO at metathesis conditions in the absence of external olefins, STO enriched in cyclopropene units (obtained by fractionation using urea) was subjected to a reaction with the Grubbs catalyst at 55 °C. Conversion of the cyclopropene units was indeed observed (26 mol% after 6 h and 40 mol% after 170 h, see Table 3), indicating that the cyclopropene units are reactive

under these conditions. ^{1}H as well as ^{13}C NMR spectra showed a large number of peaks, making identification of individual products cumbersome. However, this reaction shows that when performing cross metathesis reaction of STO with other olefins, inter molecular reactions between cyclopropene units or thermal reactions may also play a role, further complicating the chemistry and leading to a reduced selectivity of the cross-metathesis reactions.

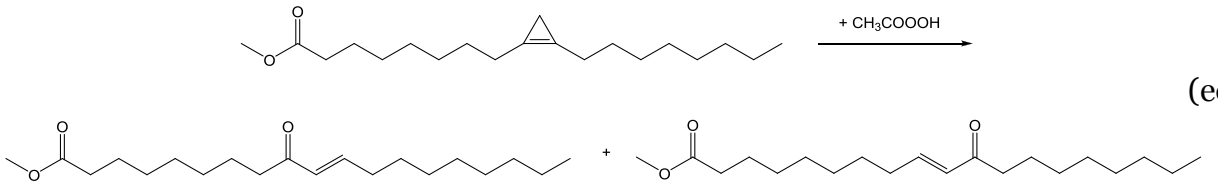
5.3.4 Oxidation reactions of STO using hydrogen peroxide at typical epoxidation and hydroxylation conditions

Oxidation reactions of STO with aqueous hydrogen peroxide were performed using a typical epoxidation protocol with MTO as the catalyst [38] and a dihydroxylation reaction using *in situ* formed performic acid [39]. For both reactions, ≥ 99 mol% conversion of the cyclopropene rings was observed (^{1}H and ^{13}C NMR). The cyclopropene unit is converted to an α,β-unsaturated ketone (enone), as shown in eq. 8.



(eq. 8)

HPLC HR-ESI-MS analysis of the *trans*-methylated product shows peaks with *m/z* values of 325.2738 and 311.2582 amu, which correspond to the enone derived from methyl sterculate and methyl malvalate, respectively. Characteristic resonances of the CH_2 moiety of the methylene branch in ^{1}H NMR were observed at δ 5.67 and 5.93 ppm. Characteristic peaks in ^{13}C NMR spectra were at about δ 123 ppm for the C=***C***H_2 group, at δ 149 ppm for the ***C***=CH_2 group and at δ 202 ppm for the carbonyl group, which is in line with literature data [49]. APT NMR of the product mixture after *trans*-methylation with methanol shows characteristic resonances of =***C***H_2 groups at about δ 123 ppm. ***C***H=***C***H groups are absent, indicating that the double bond is not located in the main fatty acid chain. The latter finding contradicts with literature data on the peracetic acid oxidation of sterculic acid. The authors reported the formation of a mixture of 9-oxo-nonadec-10-enoic acid and 11-oxo-nonadec-9-enoic acid (eq 9) [50]. However, neither mass spectra nor a rationalise for product formation are provided.



(eq. 9)

In theory, two enone regio-isomers may be formed, 9-*ene*-10-oxo-octadecanoate and 10-*ene*-9-oxo-octadecanoate. Both isomers are reported to be formed in 70% yield in equimolar amounts when oxidising STO methyl esters at ambient temperature without bubbling air for a week in the absence of catalyst [49]. We have attempted to gain insights in the ratio of the two regio-isomers by GC-MS using various derivatisation protocols (pyridinemethanol, 2-amino-2-methyl-1-propanol). Only a single peak was observed for the enone-products under the prevailing conditions. Though it is tempting to suggest that only one regio-isomer is formed, it is more likely that separation of the two regio-isomers by GC is difficult and that both are formed during reaction.

This was supported by catalytic epoxidations of the reaction mixture using KF on alumina as catalyst and *tert*-butylhydroperoxide as the oxidant in acetonitrile and subsequent analyses by GC-MS. Using this method, a single enone product peak was observed on the GC. However, the fragmentation pattern indicates the presence of two regio-isomers (Fig. 5). Besides the molecular peak at *m/z* of 340, four peaks at *m/z* 199 and 141 as well as *m/z* 185 and 155 are observed, which arise from the fragmentation of the epoxide of 9-*ene*-10-oxo- and 10-*ene*-9-oxo-octadecanoate, respectively. Thus, it is likely that two regio-isomeric enones are formed when oxidising the cyclopropene rings using conventional epoxidation methods.

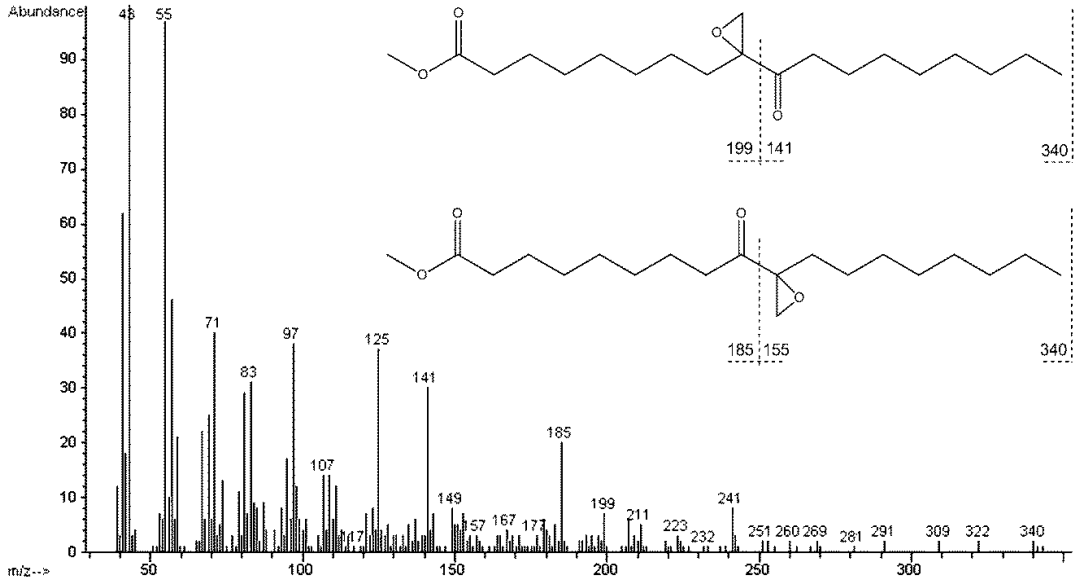
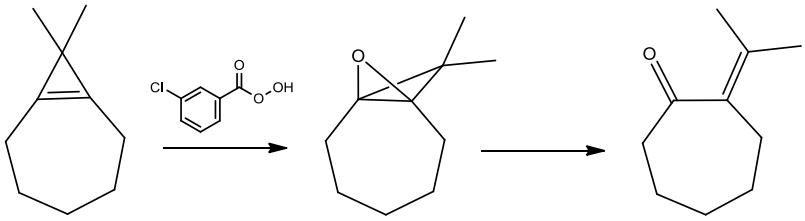


Fig. 5 Mass fragmentation pattern of the epoxidised enone units in STO

Further proof for the formation of the two regio-isomers comes from ^{13}C NMR measurements. All characteristic peaks of the enone moiety are not observed as single peaks but always a set of two is present with essentially identical intensities. This is a clear indication that two regio-isomers are formed during the reaction.

The reaction mechanism for enone formation is not known in detail. Friedrich, *et. al.* [51] postulated that the reaction likely proceeds via an intermediate oxabicyclobutane compound, see eq. 10 for a substituted cyclopropene such as 8,8-dimethylbicyclooct-1(7)-ene. The oxabicyclobutane subsequently rearranges to form

an enone. However, Okovytyy, *et. al.* [52] concluded on the basis of theoretical calculations that the intermediate oxabicyclobutane is not formed, and that the reaction proceeds via a bi-radical intermediate which forms an enone by a fast proton transfer.



(eq. 10)

NMR spectra of the reaction product also show some characteristic resonances of epoxide fragments at δ 2.79-3.15 ppm (^{1}H NMR), see Fig. 6 for details. These are likely from the epoxidation of the straight chain fatty acids with C-C double bonds (Table 1).

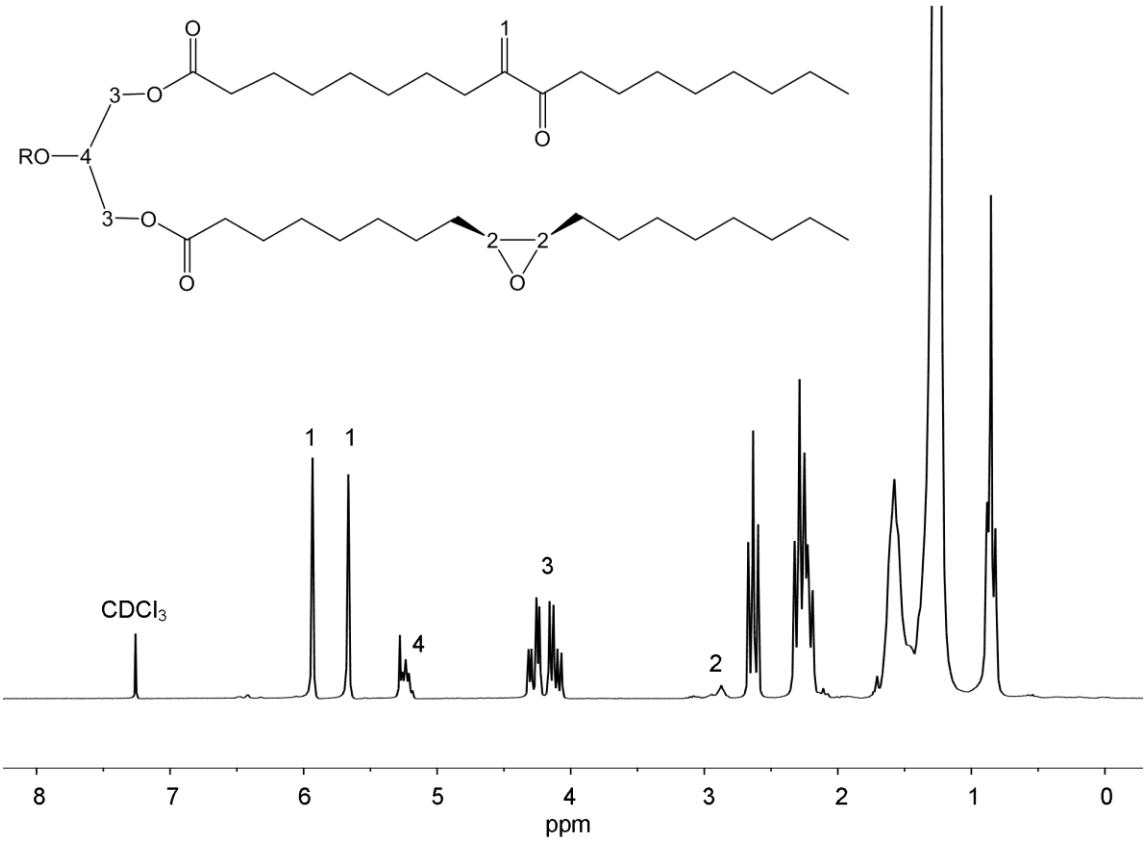
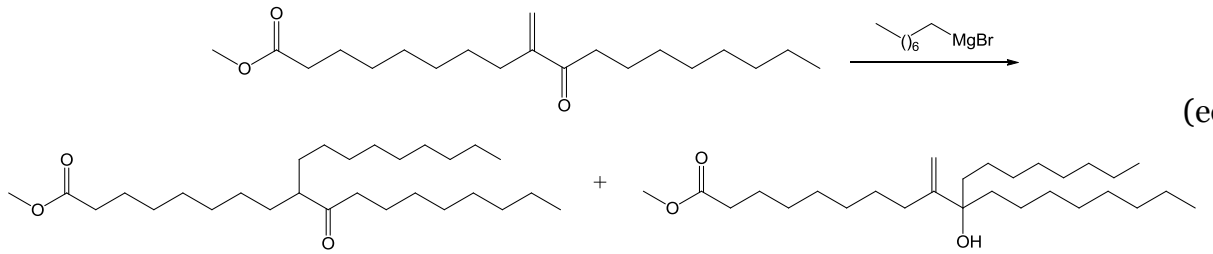


Fig. 6 ^{1}H NMR spectrum of the oxidation product of STO at typical epoxidation conditions (**5**)

A slight change of product chemoselectivity was observed when performing the reaction under dihydroxylation conditions using formic acid. At this condition, the selectivity for the enone was slightly lower (95%) and minor amounts of 1,9-nonanedioic acid and nonanoic acid were observed as well (GC-MS). The latter is indicative for the occurrence of oxidative cleavage reactions involving the cyclopropene rings. This reactivity pattern has also been observed by Ciabattoni and Kocienski [53] when using *m*-chloroperbenzoic acid as the oxidant. Nevertheless, both oxidation methods are very suitable for the selective conversion of the cyclopropene units to enones, which is an interesting functional group for further derivatisation chemistry.

5.3.5 Addition reactions of 9(10)-ene-10(9)-oxo-octadecanoate with n-octylmagnesium bromide

The STO derivative with an enone group in the fatty acid chains (**5**) obtained by oxidation with hydrogen peroxide, was subjected to a Cu-catalysed 1,4-addition reaction with n-octylmagnesiumbromide (eq. 11) using a procedure provided by Tawney [40].



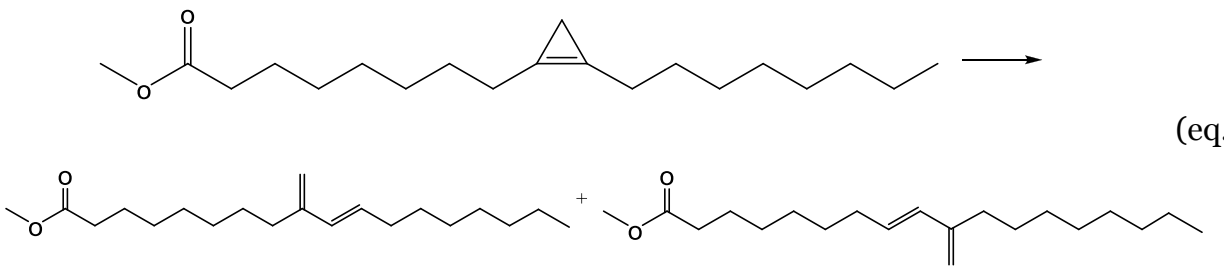
(eq. 11)

The reaction was carried out in diethyl ether at the boiling point of the solution for 3 h. Work-up gave the product as an orange coloured oil. The reaction was initially performed using 1 mol% of copper (II) chloride as the catalyst. A conversion of 82 mol% of the enone was obtained, with a 75 mol% selectivity to the 1,4-addition product and about 20 mol% to the 1,2-addition product.

Characteristic ^{1}H NMR resonances of the 1,4-addition product are at δ 2.64 ppm, from the CH group next to the carbonyl group. The 1,2-addition product shows clear peaks of the olefinic $=CH_2$ protons at δ 4.89 and 5.03 ppm. In ^{13}C NMR, the carbonyl group of the 1,4-addition product is present at δ 211-216 ppm. The CH group next to the carbonyl group of the 1,4-addition product is observed at δ 50.5 – 54.0 ppm. Meanwhile, the 1,2-addition product shows resonances of the $C=CH_2$ carbons at δ 108 and 153 ppm. The presence of the 1,2-addition product is likely due to the un-catalysed addition reaction between the reactant with octylmagnesium bromide [40]. Therefore, a reaction with 2 mol% of catalyst instead of the original 1 mol% under otherwise similar reaction conditions was employed. Improved results were obtained and the conversion of the enone was increased to 94 mol% with a selectivity of 92 mol% to the 1,4-addition product.

5.3.6 Rearrangement reactions of STO FAME to a conjugated diene with a methylene branch using homogeneous Pd catalysts

The ring opening of the cyclopropene unit in STO or derivatives to a conjugated diene with a methylene branch is an interesting reaction as the products are attractive starting material for further chemistry (eq. 12). Rearrangement reactions of STO FAME were conducted under a nitrogen atmosphere using a homogeneous palladium catalyst in a biphasic liquid-liquid system. The biphasic system consists of water and the STO FAME dissolved in a hydrocarbon solvent (heptane or cyclohexane). A water-soluble Pd catalyst (Pd-TPPTS) was used, which allows for recycle of the catalyst after the reaction by a simple phase separation. The catalyst was made *in situ* from the catalyst components ($Pd(OAc)_2$ and Na_3TPPTS). The reactions were carried out at 90 ^oC with 0.5 wt% catalyst to the ester. Catalyst performance was compared with a typical heterogeneous Pd catalyst (Pd/C 5%). The rearrangement reaction of STO FAME using a homogeneous catalyst in a biphasic solvent system has never been studied before and is an absolute novelty of this paper.



(eq. 12)

The results of the rearrangement reaction with Pd-TPPTS are given in Table 4. After 6 h, quantitative conversion of cyclopropene units was observed in both organic solvents (cyclohexane and heptane). The selectivity towards the desired product (eq 12) was > 90 mol% for both cases and slightly higher in cyclohexane than in heptane.

Table 4 Results of the rearrangement reactions[a)]

Exp	Catalyst	Solvent	Temp (^oC)	Water / solvent (v/v)	Conversion[b)] [%-mol]	Selectivity[b)] [%-mol]
1	Pd-TPPTS	Heptane	90	1	>99	90
2	Pd-TPPTS	Cyclohexane	90	1	>99	>99
3	Pd/C 5%	Heptane	150	-	75	94

[a)]Reaction time: 6h, [b)]conversion and product selectivity were calculated by ^1H NMR. Conversion is the cyclopropene conversion, selectivity is defined as the amount of rearrangement product divided by the amount of cyclopropene rings converted.

The reaction products were primarily characterised by ^{1}H, ^{13}C, and APT NMR. The characteristic peaks of the methylene branch (C=C***H***$_2$) appeared at δ 4.71-4.85 ppm in ^{1}H NMR, which is in line with literature data [16]. Meanwhile, characteristic peaks of the conjugated diene were present at around δ 113.3 (***C***H_2=C-CH=CH-), 133-128 ppm (-CH=***C***H-), and 147 ppm (CH_2=***C***-CH=CH-) in APT NMR measurements. The reaction is expected to lead to the formation of two regio-isomers, methyl 9-methylene-octadec-10-enoate and methyl 10-methylene-octadec-8-enoate. Analyses of the reaction mixture by GC-MS after various derivatisation reactions only showed a single peak. However, as the two regio-isomers are expected to have very similar physical properties, this is not conclusive evidence for the formation of a single regio-isomer. ^{13}C NMR is more informative and all characteristic peaks for the conjugated diene moiety are not observed as single peaks but double peaks with equal intensities. This is a clear indication that both regio-isomers are formed in essentially similar amounts.

A possible byproduct is a conjugated diene with a methyl branch by a subsequent rearrangement reaction (eq 1). However, this structural unit was not detected by NMR when applying the homogeneous catalysts under the prevailing reaction conditions.

To confirm the presence of a conjugated diene with a methylene branch, the reaction product was hydrogenated using palladium on carbon catalyst (10 %-wt) at a H_2 pressure of 40 bar and a temperature of 80 ^{o}C for 20 h. After reaction, the presence of the methyl peak of the new -***C***H_3 (methyl) group was observed at δ 19.7 ppm and the ***C***H group was present at δ 32.7 ppm in APT NMR spectra. Thus, it can be concluded that the rearrangement product indeed contains a conjugated diene moiety with a methylene branch. HPLC HR-ESI-MS analysis of the reaction product shows two clear peaks with *m/z* values of 309.2788 and 295.2630 amu, which indicates that the reaction is not associated with molecular weight changes, in line with the occurrence of a rearrangement reaction.

For reference, the rearrangement reaction was also performed with Pd on C at 150 ^{o}C [16]. In this case, the reaction was carried out in heptane as the solvent. Despite the elevated temperature used for this reaction compared to the reaction with the homogeneous catalyst (90 °C), the cyclopropene conversion is less than quantitative (75 mol%), though selectivity is similar to the homogeneous system. Therefore, the biphasic catalysis system using Pd-TPPTS as the catalyst appears as an attractive catalyst for these rearrangements reactions.

5.3.7 Cold flow properties

The cold flow properties of the STO and derivatives were determined using CP and PP analyses. The results of the measurements are given in Fig. 7. Modification reactions in general resulted in a reduction of the PP and CP when compared to STO FAME (**1**). The purified/de-acidified STO has a cloud and pour point (CP and PP) of -3 and -5 ^{o}C, respectively, which is in line with literature data [54]. The PP and CP for STO FAME (**1**) were both -1 ^{o}C, which is slightly higher than for STO. Despite various literature reports on the preparation of STO FAME, CP and PP values have not been reported. It is well known that the cold flow properties of methyl esters of vegetable

oils highly depend on the composition of the fatty acid chain in the oil. For example, the PP of methyl esters of rapeseed oil is -9 °C, due to a large fraction of unsaturated C18:1 and C22:1 fatty acids in the oil [55]. In contrast, both methyl esters of palm and tallow oil have a PP of 15 °C, as they contain a large fraction of saturated C16:0 fatty acids.

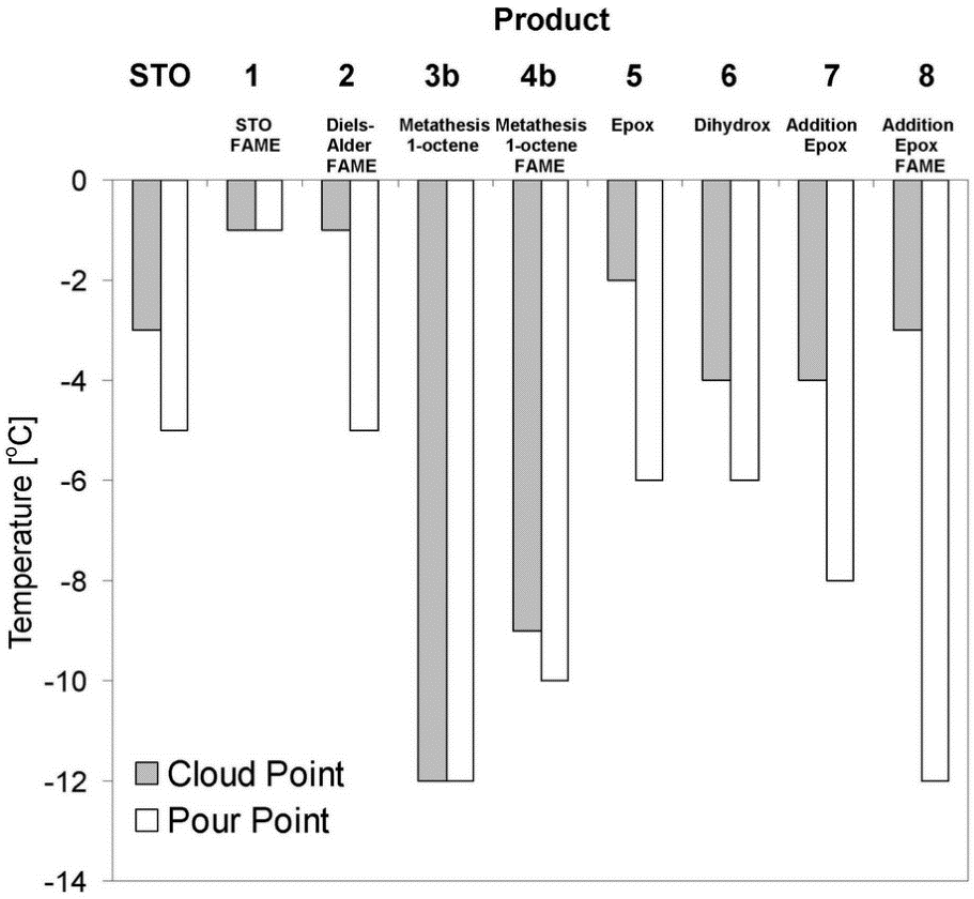


Fig. 7 Cold-flow properties of STO and derivatives

The methyl ester derivative of Diels-Alder reaction (**2**) has a CP and PP of -1 and -5 °C, which is close to that of STO but better than STO FAME (**1**). A related product containing this functional group is not reported in the literature, making comparison with literature data impossible. The product from the metathesis of 1-octene with STO (**3b**) showed a CP and PP value of -12 °C. After *trans*-esterification with methanol, the CP and PP were -9 and -10 °C (**4b**).

The epoxidation and dihydroxylation products (**5** and **6**) have similar CP and PP values of -3 and -6 °C, which is not surprising considering a similar chemoselectivity for both reactions to the enone. The values are close to those for the STO feed. Cold flow properties of enones derived from methyl sterculate and methyl malvalate are not available in the literature [49]. A structurally related fatty acid with an enone moiety has been prepared by Cádiz and coworkers [30], to be used as a novel reactive building block in polymer synthesis. However, the cold flow properties of this compound are also not reported. The addition product, **7**, has a CP and PP of -

4 and -8 °C, respectively. Structurally related compounds have been prepared, for example, by the alkoxylation of the olefinic groups in unsaturated methyl esters and triglycerides [56-59]. However, the cold flow properties of these branched fatty acid derivatives were not provided, making a comparison cumbersome.

Further improvements in cold-flow properties of the derivatives are likely possible by using fractionated STO enriched in cyclopropene units for the modification reactions. By this procedure, the amount of the fatty acids without cyclopropene rings in the products is reduced considerably. Particularly a reduction of the amount of saturated fatty acids (cf Table 1, 17 wt% palmitic acid) in crude STO is expected to have a positive effect on PP and CP of the products, as these acids are known to have a high PP and CP. These studies using fractionated STO are in progress and will be reported in due course.

5.3.8 Stability of STO during storage

The modification reactions reported here indicate that STO is an interesting starting material for the synthesis of derivatives due to the presence of highly reactive cyclopropene rings. However, this high reactivity may also lead to reactions during storage (e.g. polymerisation) and as such the storage stability may be limited. For instance, Nunn reported that sterculic acid polymerises rapidly at 96 °C in a N_2 atmosphere [20] as was observed by an increase in the molecular weight (5 times the original value after 230 min). Therefore, the chemical composition of the oil upon storage at 6 °C was investigated by ^{1}H NMR and GC analysis. The results showed that significant cyclopropene rings conversion was not observed for storage period of at least eight months at this temperature.

5.4 Conclusions

An experimental study on the chemical modifications of STO and STO FAME to prepare branched ester derivatives is reported. Excellent conversions of the cyclopropene rings under mild reaction conditions were obtained for almost all reactions performed in this study. The cold flow properties of some relevant branched oil and ester derivatives were determined and are similar or better compared to STO FAME. The high reactivity combined with a good storage stability at 6 °C, makes STO a very attractive feedstock for the production of various oleo-chemical derivatives.

5.5 List of abbreviations

STO = *Sterculia foetida* L. oil
CPEFA= cyclopropene fatty acids
CE = cyclopropene
MTO = methyl trioxorhenium
CP = cloud point
PP = pour point
APT = Attached Proton Test
1 = methyl esters of STO
2 = methyl esters of Diels-Alder reaction products
3a = product of metathesis reaction of STO with 2,3-dimethyl-2-butene
3b = product of metathesis reaction of STO with 1-octene
4a = methyl esters of **3a**
4b = methyl esters of **3b**
5 = product of epoxidation reaction
6 = product of hydroxylation reaction
7 = product of 1,4-addition reaction of STO with n-octylMgBr
8 = methyl esters of **7**
9 = methyl esters of rearrangement product

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Peer-reviewed publications:

1. **L. Daniel**, A.R. Ardiyanti, B. Schuur, R. Manurung, A.A. Broekhuis, H.J. Heeres, Synthesis and properties of highly branched *Jatropha curcas* L. oil derivatives. *Eur. J. Lipid Sci. Technol.*, **2011**, *113*, 18-30.

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4. **L. Daniel**, C.B. Rasrendra, R. Manurung, A.A. Broekhuis, H.J. Heeres, Liquid phase oxidative cleavage of levulinic acid to succinic acid using aqueous hydrogen peroxide (oral presentation), XIIth Netherlands Catalysis and Chemistry Conference, Noordwijkerhout, The Netherlands, **2011.**

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